NASA TECHNICAL NOTE

NASA TN D-5486

CALCULATED INTERACTION ENERGY AND DIPOLE MOMENT IN COLLISIONS OF TWO HYDROGEN MOLECULES

by R. W. Patch

Lewis Research Center
Cleveland, Ohio

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION • WASHINGTON, D. C. • OCTOBER 1969

1. Report No. NASA TN D-5486	2. Government Accession No.	3. Recipient's C
4. Title and Subtitle CALCULATED INTERACTION ENERGY AND DIPOLE MOMENT IN COLLISIONS OF TWO HYDROGEN MOLECULES		5. Report Date October 1969 6. Performing Organization Code
7. Author(s) R. W. Patch		8. Performing Organization Report No. E-5075
9. Performing Organization Name and Address Lewis Research Center National Aeronautics and Space Administration Cleveland, Ohio 44135		10. Work Unit No. 122-28 11. Contract or Grant No. 13. Type of Report and Period Covered Technical Note
12. Sponsoring Agency Name and Address National Aeronautics and Space Administration Washington, D.C. 20546		14. Sponsoring Agency Code

15. Supplementary Notes

16. Abstract

Calculations were carried out using orthogonalized valence-bond theory. Methods of calculating accurate values of integrals are given. Linear, planar perpendicular, quadrilateral, and nonplanar perpendicular configurations were included with intermolecular distances from 2.5 to 5.5 bohrs (0.13 to 0.29 nm) and two internuclear distances. The interaction energies obtained appear to be valid for intermolecular distances less than 4.5 bohr (0.24 nm) but are too large at appreciably greater intermolecular distances due to insufficient allowance for electron correlation in the wave function. A simple average interaction energy (Morse potential) for practical applications is cited which correlates calculations in this report and experiments.

17. Key Words *(Suggested by Author(s))*
Dipole moment
Hydrogen
Intermolecular energy
Molecular integrals

18. Distribution Statement
Unclassified - unlimited

19. Security Classif. (of this report)	20. Security Classif. (of this page)	21. No. of Pages	22. Price*
Unclassified	Unclassified	44	$3.00

*For sale by the Clearinghouse for Federal Scientific and Technical Information
Springfield, Virginia 22151

CONTENTS

CALCULATED INTERACTION ENERGY AND DIPOLE MOMENT IN COLLISIONS OF TWO HYDROGEN MOLECULES

by R. W. Patch

Lewis Research Center

SUMMARY

Ab initio calculations of the interaction energy and electric dipole moment of two colliding hydrogen molecules were carried out on a digital computer using the orthogonalized valence-bond theory of McWeeny. Methods of calculating accurate values of all molecular integrals are given in some detail for cases with equal or unequal orbital exponents (screening constants). Linear, planar perpendicular, quadrilateral, and nonplanar perpendicular configurations were included with intermolecular distances from 2.5 to 5.5 bohrs (0.13 to 0.29 nm) and internuclear distances in the hydrogen molecules of 1.401446 and 1.450000 bohrs (0.0741599 and 0.0767292 nm). A weighted average of the interaction energies of the four equilibrium configurations was then taken for each intermolecular distance.

The interaction energies obtained appear to be valid for intermolecular distances less than 4.5 bohrs (0.24 nm) but are too large at appreciably greater intermolecular distances because of insufficient allowance for electron correlation in the wave function. A simple average interaction energy (Morse potential) for practical applications is cited which correlates experiments for intermolecular distances greater than 4.0 bohrs (0.21 nm) and correlates the calculations in this report for intermolecular distances less than 4.0 bohrs (0.21 nm).

The electric dipole moments obtained with the full valence-bond model appear to be approximately correct for intermolecular distances up to 4.5 bohrs (0.24 nm), but for appreciably larger distances are too small because of limitations of the model. Derivatives of the electric dipole moment with respect to the internuclear distances were also calculated.

INTRODUCTION

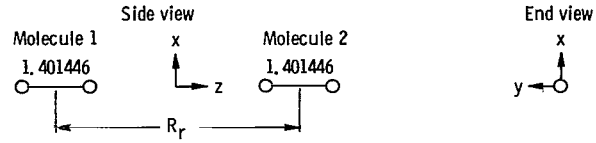
In high-temperature propulsion devices such as gas-core nuclear rockets, an important mechanism of heat transfer is radiant energy exchange between volumes of gas and between the gas and the wall (refs. 1 and 2). When such devices use high pressure hydrogen, it is necessary to know the strength of pressure-induced infrared absorption to calculate the heat transfer. This strength depends on the interaction energy and electric dipole moment of two colliding hydrogen molecules (H_2 - H_2) and has not been measured much above room temperature. At the temperatures that occur in these high-temperature propulsion devices, smaller intermolecular distances become important in calculating the strength.

The object of the work herein described was to calculate interaction energies and electric dipole moments for small intermolecular distances. The results should also be useful for calculating high-temperature transport properties of gases containing hydrogen and for calculating the equation of state of high-pressure hydrogen for application to light-gas guns.

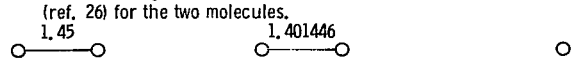
Past work on H_2 - H_2 interaction energy may be divided into ab initio calculations, semiempirical calculations, and experiments. These three types of work will be discussed in subsequent paragraphs. In none of these interaction energy calculations was the dipole moment calculated, but the dipole moment by itself was calculated in a semiempirical calculation by another investigator.

Ab initio calculations for H_2 - H_2 have been carried out in 10 studies. For those unfamiliar with this type of calculation, a review of the methods used has been given by Slater (ref. 3). The H_2 - H_2 calculations may be divided into two groups: those where approximations were used for some molecular integrals, and those where all molecular integrals were calculated accurately. Since the interaction energy is a sensitive function of the molecular integrals, this is an important distinction. Griffing and Vanderslice (ref. 4) calculated energy of linear H_4. Griffing and Maček (ref. 5) calculated the energy of square H_4. Ruffa and Griffing (ref. 6) computed the interaction energy of linear H_2 - H_2. All three of these studies used approximations for some of the molecular integrals. Accurate values of the integrals were used by Taylor (ref. 7) for the energy of linear H_4, Magnasco and Musso (refs. 8 to 12) for the energy of quadrilateral and skewed H_2 - H_2, Magnasco, Musso, and McWeeny (ref. 13) for the energy of quadrilateral and skewed H_2 - H_2, and by Schwartz and Schaad (ref. 14) for the energy of linear H_4. None of the studies using accurate values of the integrals were done for a sufficient number of configurations to permit proper averaging of the interaction energies over nuclear configuration space, although this is necessary for practical applications.

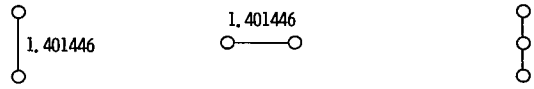
Semiempirical calculations of H_2 - H_2 interaction energy have been made by



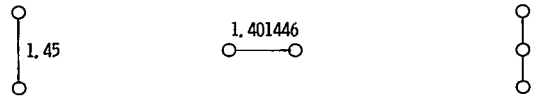
(a) Linear configuration A with equilibrium internuclear distances (ref. 26) for the two molecules.



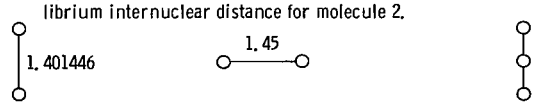
(b) Linear configuration B with greater-than-equilibrium internuclear distance for molecule 1 and equilibrium internuclear distance for molecule 2.



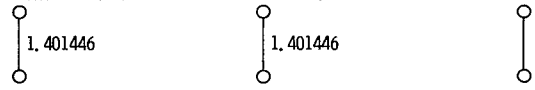
(c) Planar perpendicular configuration C with equilibrium internuclear distances for the two molecules.



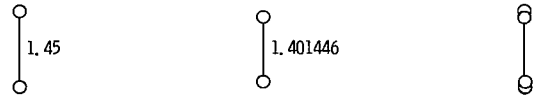
(d) Planar perpendicular configuration D with greater-than-equilibrium internuclear distance for molecule 1 and equilibrium internuclear distance for molecule 2.



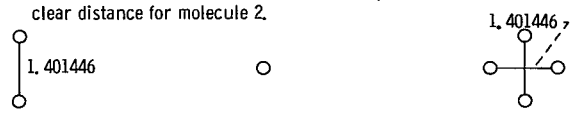
(e) Planar perpendicular configuration E with equilibrium internuclear distance for molecule 1 and greater-than-equilibrium internuclear distance for molecule 2.



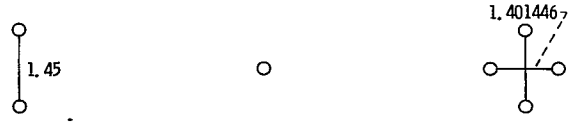
(f) Quadrilateral configuration F with equilibrium internuclear distances for both molecules.



(g) Quadrilateral configuration G with greater-than-equilibrium internuclear distance for molecule 1 and equilibrium internuclear distance for molecule 2.



(h) Nonplanar perpendicular configuration H with equilibrium internuclear distances for both molecules.



(i) Nonplanar perpendicular configuration I with greater-than-equilibrium internuclear distance for molecule 1 and equilibrium internuclear distance for molecule 2.

Figure 1. - Nine configurations of two hydrogen molecules used in calculations. Intermolecular distance R_r had values of 2.5, 3.5, 4.5, and 5.5 bohrs (1 bohr = 5.29167×10^{-11} m). Internuclear distances in the figure are in bohrs (not to scale).

Margenau (ref. 15) (corrected by Evett and Margenau in ref. 16), Mason and Hirschfelder (ref. 17), Vanderslice and Mason (ref. 18), and Abrams, Patel, and Ellison (ref. 19). A semiempirical calculation of the H_2 - H_2 electric dipole moment has been made by Van Kranendonk and Kiss (ref. 20).

Experiments pertinent to H_2 - H_2 average interaction energy involve hydrogen viscosity and equation of state measurements. A large number of measurements of these two types have been made, but most were not at high enough temperatures to give any indication of the H_2 - H_2 interaction energy at small intermolecular distances. However, Guevara and Wageman (ref. 21) measured hydrogen viscosity to 2340 K. Fisher (ref. 22) fit Guevara and Wageman's data together with lower temperature viscosity and equation-of-state data with a Morse intermolecular potential, which should therefore be valid down to an intermolecular distance of 4.0 bohrs (0.21 nm).

In this study a full valence-bond, ab initio calculation of H_2 - H_2 interaction energy and electric dipole moment was carried out with accurate values for all molecular integrals. In order to cover nuclear configuration space, linear, planar perpendicular, quadrilateral, and nonplanar perpendicular configurations (see fig. 1) were included with intermolecular distances from 2.5 to 5.5 bohr (0.13 to 0.29 nm). In four of the configurations (fig. 1(a), (c), (f), and (h)) both H_2 molecules had equilibrium internuclear distances. The average H_2 - H_2 interaction energy was then calculated for a given intermolecular distance by taking weighted averages of the interaction energies of these four configurations. In five of the configurations (fig. 1(b), (d), (e), (g), and (i)) one of the H_2 molecules had a nonequilibrium internuclear distance so that the derivatives of the dipole moment with respect to internuclear distance could be calculated from the electric dipole moments of all nine configurations. The calculations in this report differ from those of references 9 and 10 in the configurations calculated and in mathematical details.

The author is indebted to Professor V. Magnasco of the Istituto di Chimica Industriale dell'Universita, Genoa, for providing listings and a deck of various computer programs for evaluating molecular integrals. Although these programs were not used for this report, they were useful for checking and provided ideas for the programs that were used.

ANALYSIS

Model and Configurations

The interaction of two H_2 molecules may be calculated by the orthogonalized valence-bond theory of McWeeny (refs. 23 and 24), which utilizes symmetrically orthogonalized atomic orbitals in the Born-Oppenheimer approximation. In this method

orthogonalized orbitals are formed from linear combinations of atomic orbitals. These are multiplied by spin eigenfunctions to give orthogonalized spin-orbitals. Formal orthogonalized valence-bond structures are formed from linear combinations of anti-symmetrized products of the orthogonalized spin-orbitals. The system wave function consists of linear combinations of these structures. This involved procedure merely amounts to taking the proper linear combination of the octuple products of four atomic orbitals and four spin eigenfunctions. This method has the advantage that it allows full configuration interaction without serious complexity. It has previously been applied to the interaction of two H_2 molecules by Magnasco and Musso (refs. 8 to 10).

The simplest possible model for a full valence-bond calculation was chosen. The two H_2 molecules were assumed to be in the ground electronic state so that for infinite separation each of the H_2 molecules could be described by the covalent-ionic valence-bond model of Weinbaum (ref. 25). In Weinbaum's model, two 1s atomic orbitals with equal orbital exponents (screening constants) were used. To be consistent, in the full valence-bond model used for H_2 - H_2 a set of four 1s atomic orbitals χ_p centered on the protons was selected. The respective orbital exponents ζ_p were assumed to be the same as in the respective isolated H_2 molecules described by the Weinbaum model. If both molecules had the same internuclear distances, all orbital exponents were equal. If the two molecules had different internuclear distances, two orbital exponents had one value, and the other two had a different value. The four normalized 1s atomic orbitals χ_p were

$$\chi_p(i) = \left(\frac{\zeta_p^3}{\pi}\right)^{1/2} e^{-\zeta_p r_{pi}} \qquad p = a, b, c, d \tag{1}$$

where the i in parentheses indicates the i^{th} electron, and r_{pi} is the distance between proton p and electron i (symbols are given in appendix A). An orbital $\chi_p(i)$, of course, reduces to the wave function for the ground state of an H atom if $\zeta_p = 1.0$ $bohr^{-1}$.

Four equilibrium configurations (fig. 1(a), (c), (f), and (h)) were chosen so that interaction energy could be conveniently averaged over molecular orientations. The experimental equilibrium internuclear distance of 1.401446 bohrs (0.0741599 nm) for H_2 (refs. 26 and 27) was used rather than Weinbaum's value of 1.4166 bohrs (0.074962 nm) (ref. 25) because of the ultimate application of this report to pressure induced absorption.

The other five configurations in figure 1 possessed a nonequilibrium internuclear distance so the derivatives of the electric dipole moment with respect to internuclear distance could be calculated from the nine configurations.

In all nine configurations the intermolecular distance R_r was varied. It had values of 2.5, 3.5, 4.5, and 5.5 bohrs (1 bohr = 0.0529167 nm).

Energy and Interaction Energy

To find the electronic energy of the H_2 - H_2 complex, a Löwdin transformation was performed on the orbitals, resulting in orthogonalized orbitals. Formal orthogonalized valence-bond structures were formed, and the matrix elements of the Hamiltonian were found. An eigenvalue problem was then solved to obtain the electronic energy. The nuclear repulsion energy was added to this to get the energy of the complex. The energies of the two infinitely separated H_2 molecules were subtracted from the energy of the complex to yield the interaction energy. These steps are given in the following paragraphs.

Löwdin transformation. - The symmetrical orthogonalization procedure of Löwdin (ref. 28) was applied to the χ_p. The overlap integral is

$$S_{pq} \equiv \int \chi_p(1)\chi_q(1)dv_1 \tag{2}$$

Let

$$w_{pq} \equiv \frac{\zeta_p + \zeta_q}{2} R_{pq} \tag{3}$$

where R_{pq} is the distance between protons p and q. If $\zeta_p = \zeta_q$, S_{pq} is given by Slater (ref. 3, p. 50). If $\zeta_p \neq \zeta_q$,

$$S_{pq} = \frac{\sqrt{\zeta_p^3 \zeta_q^3} R_{pq}^3}{4} \left[\frac{e^{\check{q}} - e^{-\check{q}}}{\check{q}} \frac{2}{w_{pq}^2} \left(1 + w_{pq} + \frac{w_{pq}^2}{2} \right) + e^{-\check{q}} \left(\frac{1}{\check{q}} + \frac{2}{\check{q}^2} + \frac{2}{\check{q}^3} \right) + e^{\check{q}} \left(-\frac{1}{\check{q}} + \frac{2}{\check{q}^2} - \frac{2}{\check{q}^3} \right) \right] \frac{e^{-w_{pq}}}{w_{pq}} \tag{4}$$

where

$$\check{q} \equiv \frac{\zeta_p - \zeta_q}{2} R_{pq} \tag{5}$$

It is desired to find the Löwdin transformation matrix $\underline{M_\chi^{-1/2}}$ such that

$$\underline{\chi'} = \underline{\chi}\,\underline{M_\chi^{-1/2}} \tag{6}$$

where $\underline{\chi}$ is a row vector with elements χ_p, and $\underline{\chi'}$ is a row vector of the four orthogonalized orbitals χ'_p. First the eigenvalue problem

$$\underline{\tilde{U}}\,\underline{S}\,\underline{U} = \underline{d} \tag{7}$$

is solved, where $\underline{S}$ is a matrix with elements S_{pq}. The matrix $\underline{d}$ is diagonal, with eigenvalues as diagonal elements. Thus

$$\underline{d}^{-1/2} = \begin{bmatrix} d_{11}^{-1/2} & 0 & 0 & 0 \\ 0 & d_{22}^{-1/2} & 0 & 0 \\ 0 & 0 & d_{33}^{-1/2} & 0 \\ 0 & 0 & 0 & d_{44}^{-1/2} \end{bmatrix} \tag{8}$$

Finally,

$$\underline{M_\chi^{-1/2}} = \underline{U}\,\underline{d}^{-1/2}\,\underline{\tilde{U}} \tag{9}$$

Use of equation (6) then accomplishes the Löwdin transformation to obtain $\underline{\chi'}$.

Formal orthogonalized valence-bond structures. - To produce the proper antisymmetry, the χ'_p are combined in antisymmetrized products of orthogonalized spin-orbitals.

$$(pq\overline{rs}) \equiv (4!)^{-1/2} \det\left[\chi'_p(1)\alpha(1),\ \chi'_q(2)\alpha(2),\ \chi'_r(3)\beta(3),\ \chi'_s(4)\beta(4)\right] \tag{10}$$

where $\alpha(1)$ is the spin eigenfunction of electron 1 with the component of spin angular momentum along the axis of quantization equal to $\hbar/2$, and $\beta(3)$ is the spin eigenfunction of electron 3 with the component of spin angular momentum along the axis of quantization equal to $-\hbar/2$. The shorthand notation is given on the left side of equation (10), wherein a bar indicates β spin and no bar indicates α spin. To facilitate computing for some purposes, the $(pq\overline{rs})$ are arranged in dictionary order in a 6 by 6 matrix (ref. 29).

$$\begin{bmatrix} (ab\overline{ab}) & (ab\overline{ac}) & (ab\overline{ad}) & (ab\overline{bc}) & (ab\overline{bd}) & (ab\overline{cd}) \\ (ac\overline{ab}) & (ac\overline{ac}) & (ac\overline{ad}) & (ac\overline{bc}) & (ac\overline{bd}) & (ac\overline{cd}) \\ (ad\overline{ab}) & (ad\overline{ac}) & (ad\overline{ad}) & (ad\overline{bc}) & (ad\overline{bd}) & (ad\overline{cd}) \\ (bc\overline{ab}) & (bc\overline{ac}) & (bc\overline{ad}) & (bc\overline{bc}) & (bc\overline{bd}) & (bc\overline{cd}) \\ (bd\overline{ab}) & (bd\overline{ac}) & (bd\overline{ad}) & (bd\overline{bc}) & (bd\overline{bd}) & (bd\overline{cd}) \\ (cd\overline{ab}) & (cd\overline{ac}) & (cd\overline{ad}) & (cd\overline{bc}) & (cd\overline{bd}) & (cd\overline{cd}) \end{bmatrix} \tag{11}$$

For our purposes we will regard the $(pq\overline{rs})$ as a 36-element row vector with the elements numbered down the first column in equation (11), then down the second column, etc. When numbered in this way, set

$$\varphi_i = (pq\overline{rs}) \qquad i = 1, 2, \ldots, 36 \tag{12}$$

where p, q, $\overline{r}$, and $\overline{s}$ are given in equation (11).

The formal orthogonalized valence-bond structures ψ_j are linear combinations of the φ_i. These ψ_j are eigenfunctions of the total electron spin with total spin angular momentum of 0 and component of the total spin angular momentum along the axis of quantization of 0. They have been given by Magnasco and Musso (ref. 9) and in the present nomenclature are

$$\left.\begin{aligned}
\psi_1 &= \tfrac{1}{2}(-\varphi_{11} - \varphi_{16} - \varphi_{21} - \varphi_{26}) & \psi_{11} &= 2^{-1/2}(\varphi_5 + \varphi_{25}) \\
\psi_2 &= \tfrac{1}{2}(\varphi_6 - \varphi_{16} - \varphi_{21} + \varphi_{31}) & \psi_{12} &= 2^{-1/2}(\varphi_{12} + \varphi_{32}) \\
\psi_3 &= 2^{-1/2}(-\varphi_{10} - \varphi_{20}) & \psi_{13} &= 2^{-1/2}(-\varphi_2 - \varphi_7) \\
\psi_4 &= 2^{-1/2}(-\varphi_{17} - \varphi_{27}) & \psi_{14} &= 2^{-1/2}(-\varphi_{30} - \varphi_{35}) \\
\psi_5 &= 2^{-1/2}(-\varphi_9 - \varphi_{14}) & \psi_{15} &= -\varphi_8 \\
\psi_6 &= 2^{-1/2}(-\varphi_{23} - \varphi_{28}) & \psi_{16} &= -\varphi_{15} \\
\psi_7 &= 2^{-1/2}(-\varphi_4 - \varphi_{19}) & \psi_{17} &= -\varphi_{22} \\
\psi_8 &= 2^{-1/2}(\varphi_{18} + \varphi_{33}) & \psi_{18} &= -\varphi_{29} \\
\psi_9 &= 2^{-1/2}(\varphi_3 + \varphi_{13}) & \psi_{19} &= \varphi_1 \\
\psi_{10} &= 2^{-1/2}(-\varphi_{24} - \varphi_{34}) & \psi_{20} &= \varphi_{36}
\end{aligned}\right\} \tag{13}$$

where formal singly polar and doubly polar structures are included. All ψ_i are orthonormal (see ref. 30) except ψ_1 and ψ_2. These may be made orthonormal by the Schmidt orthogonalization procedure, which results in replacing ψ_2 in equation (13) by a new ψ_2 such that

$$\psi_2 = \frac{\varphi_6}{3^{1/2}} + \frac{\varphi_{11}}{2 \cdot 3^{1/2}} - \frac{\varphi_{16}}{2 \cdot 3^{1/2}} - \frac{\varphi_{21}}{2 \cdot 3^{1/2}} + \frac{\varphi_{26}}{2 \cdot 3^{1/2}} + \frac{\varphi_{31}}{3^{1/2}} \tag{14}$$

Equations (13) (excluding ψ_2) and (14) can be represented by

$$\underline{\psi} = \underline{\varphi}\,\underline{V} \tag{15}$$

where $\underline{V}$ is a 36 by 20 matrix. The wave function of the system was taken as

$$\Psi = \underline{\psi}\,\underline{C} \tag{16}$$

where $\underline{C}$ is a column vector determined by minimizing the electronic energy E_e. This is accomplished by the variation principle for orthonormal functions (ref. 31) which poses an eigenvalue problem

$$\underline{H}\,\underline{C} = E_e\,\underline{C} \tag{17}$$

where the smallest of the several eigenvalues E_e is the ground state electronic energy, and $\underline{H}$ is a matrix whose elements are given in the following sections.

Matrix elements of the Hamiltonian. - The Hamiltonian operator for the electronic energy in atomic units with the hartree as the unit of energy is

$$\hat{H} = \sum_{i=1}^{4} -\frac{1}{2}\nabla_i^2 + \sum_{i=1}^{4}\sum_{p=a}^{d} -\frac{1}{r_{pi}} + \sum_{i=2}^{4}\sum_{j=1}^{i-1}\frac{1}{r_{ij}} \tag{18}$$

Here ∇_i^2 is the Laplacian operator for the coordinates of electron i, and the p summation is over protons a, b, c, and d. The elements of the $\underline{H}$ matrix in equation (17) are then

$$H_{nk} = \int \psi_n^* \hat{H} \psi_k d\tau \tag{19}$$

where τ includes electron configuration and spin coordinates. From equations (15) and (19)

$$\underline{H} = \underline{\tilde{V}}\,\underline{H_{\varphi}}\,\underline{V} \tag{20}$$

where

$$(H_{\varphi})_{ij} = \int \varphi_i \hat{H} \varphi_j d\tau \tag{21}$$

The matrix elements $(H_{\varphi})_{ij}$ can be found from Slater's rules (ref. 30 after correction of a typographical error) if two kinds of integrals are known

$$\overline{F}_{ij} \equiv \int \chi_i'(1) \left(-\frac{1}{2} \nabla_1^2 + \sum_{p=a}^{d} -\frac{1}{r_{p1}} \right) \chi_j'(1) dv_1 \tag{22}$$

$$\overline{G}_{ijk\ell} \equiv \iint \chi_i'(1)\chi_j'(1)\chi_k'(2)\chi_\ell'(2) \frac{1}{r_{12}} dv_1\, dv_2 \tag{23}$$

where r_{12} is the distance from electron 1 to electron 2, dv_1 is the volume element for electron 1, and dv_2 is the volume element for electron 2. From equations (6), (22), and (23)

$$\overline{F}_{ij} = \sum_{k=1}^{4} \left(M_{\chi}^{-1/2}\right)_{ki} \sum_{\ell=1}^{4} \left(M_{\chi}^{-1/2}\right)_{\ell j} \left(K_{k\ell} + \sum_{p=a}^{d} L_{k\ell p} \right) \tag{24}$$

$$\overline{G}_{ijk\ell} = \sum_{m=1}^{4} \left(M_{\chi}^{-1/2}\right)_{mi} \sum_{n=1}^{4} \left(M_{\chi}^{-1/2}\right)_{nj} \sum_{o=1}^{4} \left(M_{\chi}^{-1/2}\right)_{ok} \sum_{p=1}^{4} \left(M_{\chi}^{-1/2}\right)_{p\ell} G_{mnop} \tag{25}$$

where

$$K_{kl} \equiv \int \chi_k(1) \left(-\frac{1}{2}\nabla_1^2\right) \chi_l(1) dv_1 \tag{26}$$

$$L_{jkp} \equiv \int \chi_j(1)\chi_k(1)\left(\frac{-1}{r_{p1}}\right) dv_1 \tag{27}$$

$$G_{mnop} \equiv \iint \chi_m(1)\chi_n(1)\chi_o(2)\chi_p(2) \frac{1}{r_{12}} dv_1 dv_2 \tag{28}$$

The methods of evaluating K_{kl}, L_{jkp}, and G_{mnop} are given in appendixes B to D, respectively.

Energies. - The energy E is the electronic energy plus the nuclear repulsion energy.

$$E = E_e + \frac{1}{R_{ab}} + \frac{1}{R_{ac}} + \frac{1}{R_{ad}} + \frac{1}{R_{bc}} + \frac{1}{R_{bd}} + \frac{1}{R_{cd}} \tag{29}$$

The interaction energy E_{int} is the energy E minus the energies $E_m(r_1)$ and $E_m(r_2)$ of the isolated H_2 molecules with internuclear distances r_1 and r_2, respectively.

$$E_{int} = E - E_m(r_1) - E_m(r_2) \tag{30}$$

The diatomic internuclear distances used in equation (30) were the same as in the H_2 - H_2 complex (see fig. 1). The H_2 energies $E_m(r)$ were calculated for the covalent-ionic valence-bond model (ref. 25).

Average Interaction Energy

The average interaction energy $\overline{E}_{int}$ of two H_2 molecules is, to a first approximation, the interaction energy for equilibrium diatomic internuclear distances averaged over all possible orientations of the two H_2 molecules. Since only four configurations

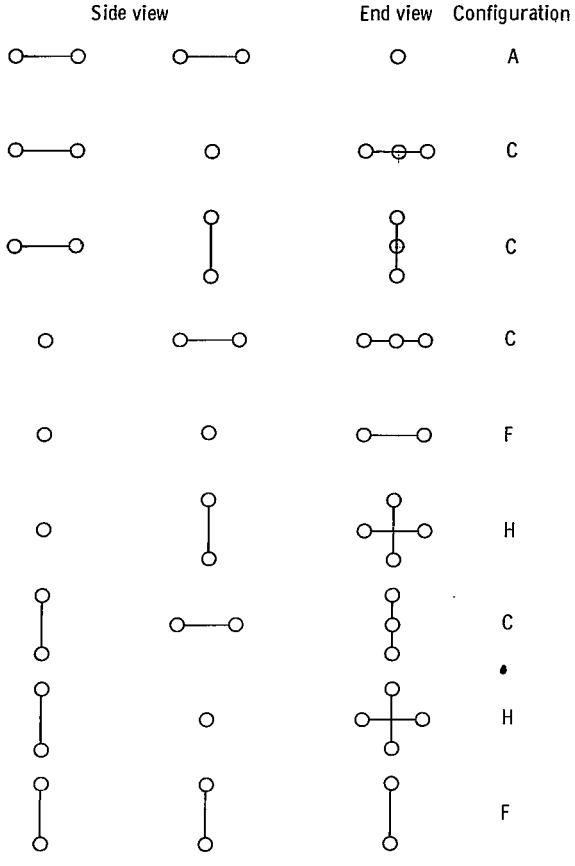


Figure 2. - Nine equilibrium orientations with equal probability if differences in interaction energy are neglected. These orientations were used to determine weighting factors for calculating average interaction energy (see fig. 4). Configuration in figure 1 to which each of the orientations shown is equivalent is given at the right.

with equilibrium diatomic internuclear distances were considered in this report, an additional approximation was necessary. Instead of using all possible orientations, the nine orientations in figure 2 were used. These are equally probable if differences in interaction energy are neglected, and each is equivalent to configurations A, C, F, or H (see fig. 1). Hence,

$$\overline{E}_{int} = \frac{1}{9} E_{int,a} + \frac{4}{9} E_{int,c} + \frac{2}{9} E_{int,f} + \frac{2}{9} E_{int,h} \tag{31}$$

where the constants are weighting factors. A better value of $\overline{E}_{int}$ can be found by including Boltzmann factors in the weighting (ref. 32, pp. 921-922), but then $\overline{E}_{int}$ would be complicated by temperature dependence.

Electric Dipole Moment

Calculation of the dipole moment requires an electron population analysis in terms of the original nonorthogonal orbitals χ_p. A column vector $\underline{C'}$ may be defined by

$$\Psi = \underline{\varphi C'} \tag{32}$$

From equations (15), (16), and (32)

$$\underline{C'} = \underline{V}\,\underline{C} \tag{33}$$

The electron population in the orbital density $\chi_p\chi_q$ irrespective of spin state is

$$P'_{mn} = \sum_{r=1}^{36} C'_r \sum_{s=1}^{36} C'_s \left(n_{rs}^{m\alpha n\alpha} + n_{rs}^{m\beta n\beta} \right) \tag{34}$$

where $n_{rs}^{m\alpha n\alpha}$ and $n_{rs}^{m\beta n\beta}$ are coefficients of spin-orbital products and are called $n_{rs}^{\mu\nu}$ by Magnasco and Musso (refs. 8 and 29), who give rules for evaluating them (ref. 29).

The electron population in the orbital density $\chi_p\chi_q$ irrespective of spin state is (ref. 8)

$$P_{pq} = \sum_{m=1}^{4} \left(M_\chi^{-1/2} \right)_{pm} \sum_{n=1}^{4} P'_{mn} \left(M_\chi^{-1/2} \right)_{qn} \tag{35}$$

The normalized 1-electron population is

$$\mathscr{P}_{pq} = P_{pq} S_{pq} \tag{36}$$

where the four diagonal elements of the matrix $\underline{\mathscr{P}}$ give the atomic populations and the off-diagonal elements give the overlap populations. For instance, the population in the overlap between orbitals centered on protons a and b is $\mathscr{P}_{ab} + \mathscr{P}_{ba}$. The elements of the $\underline{\mathscr{P}}$ matrix, of course, add to 4, the number of electrons.

To find the dipole moment from $\underline{\mathscr{P}}$, it is necessary to know locations of the atomic charge centers and the overlap charge centers. Cartesian coordinates with the origin half way between the molecules were chosen (see fig. 1(a)). The j^{th} Cartesian coordinate of either type of charge center was designated $\overline{C}_{pqj}$, where p and q correspond to

the two orbitals χ_p and χ_q involved in an overlap charge or where p and q are equal and correspond to the one orbital involved in an atomic charge. The C_{ppj} for atomic charges are, of course, identical to the coordinates of the protons C_{pj}. For overlap charges

$$\overline{C}_{pqj} = \left(\frac{1}{2} - \Delta_{pq}\right) C_{pj} + \left(\frac{1}{2} + \Delta_{pq}\right) C_{qj} \tag{37}$$

where Δ_{pq} is the displacement of the overlap charge center from the p-q geometric center, measured in the direction from p towards q and expressed in units of R_{pq}. If $\zeta_p = \zeta_q$, $\Delta_{pq} = 0$ by symmetry. If $\zeta_p \neq \zeta_q$

$$\Delta_{pq} = \frac{R_{pq}^3 e^{-w_{pq}}}{8 S_{pq} w_{pq}^2} \sqrt{\zeta_p^3 \zeta_q^3} \left\{ \left[e^{-\check{q}} \left(-\frac{1}{\check{q}} - \frac{1}{\check{q}^2} \right) - e^{\check{q}} \left(\frac{1}{\check{q}} - \frac{1}{\check{q}^2} \right) \right] \left(\frac{6}{w_{pq}^2} + \frac{6}{w_{pq}} + 3 + w_{pq} \right) \right.$$
$$\left. + \left[e^{-\check{q}} \left(\frac{1}{\check{q}} + \frac{3}{\check{q}^2} + \frac{6}{\check{q}^3} + \frac{6}{\check{q}^4} \right) + e^{\check{q}} \left(\frac{1}{\check{q}} - \frac{3}{\check{q}^2} + \frac{6}{\check{q}^3} - \frac{6}{\check{q}^4} \right) \right] (1 + w_{pq}) \right\} \tag{38}$$

The j^{th} component of the dipole moment in atomic units is then

$$\mu_j = - \sum_{p=1}^{4} \sum_{q=1}^{4} \mathscr{P}_{pq} \overline{C}_{pqj} \tag{39}$$

By symmetry, only the z component may be nonzero.

Computer Programs

Calculation of the energy, interaction energy, and electric dipole moment of H_2 - H_2 was programmed in FORTRAN IV, IBM version 13, for an IBM 7094 digital computer. One program calculated all the three- and four-center molecular integrals and had an average running time of 8.09 minutes per case. A second program did the remaining calculations and had an average running time of 0.38 minute per case.

RESULTS AND DISCUSSION

In this section results are given for the covalent-ionic valence-bond model of H_2. These results are then used to calculate H_2 - H_2 interaction energy and electric dipole moment. Comparisons are made with the results of other investigators.

Covalent-Ionic Valence-Bond Model of H_2

The treatment of the covalent-ionic valence-bond model of H_2 given by Weinbaum (ref. 25) was reformulated so values of ζ and E_m could be calculated for given internuclear distance r. The computer program of Dellepiane, Ferro, and Magnasco (ref. 33) was used to calculate the necessary integral logarithms. The results are given in table I. For an internuclear distance of 1.4166 bohrs (0.074962 nm), we got

TABLE I. - ENERGY AND ORBITAL EXPONENT FOR COVALENT-IONIC VALENCE-BOND MODEL OF HYDROGEN MOLECULE

Internuclear distance, r		Energy, E_m		Orbital exponent, ζ	
bohrs	m	hartrees	J	$bohrs^{-1}$	m^{-1}
1.300000	6.8792×10^{-11}	-1.14462	-4.9899×10^{-18}	1.2240	2.3131×10^{10}
[a]1.401446	7.4160	-1.14779	-5.0037	1.2002	2.2681
[b]1.416600	7.4962	-1.14790	-5.0042	1.1970	2.2620
1.450000	7.6729	-1.14787	-5.0041	1.1896	2.2481
1.530000	8.0963	-1.14646	-4.9979	1.1730	2.2167

[a]Gives minimum energy based on spectroscopic data (ref. 26).
[b]Gives minimum energy for this model (ref. 25).

$\zeta = 1.197$ $bohrs^{-1}$, but Weinbaum got $\zeta = 1.193$ $bohrs^{-1}$. However, our energy agrees exactly with Weinbaum's. The energy was not very sensitive to the value of ζ. Values of E_m and ζ from table I were used in the following H_2 - H_2 calculations.

H_2 - H_2 Energy and Interaction Energy

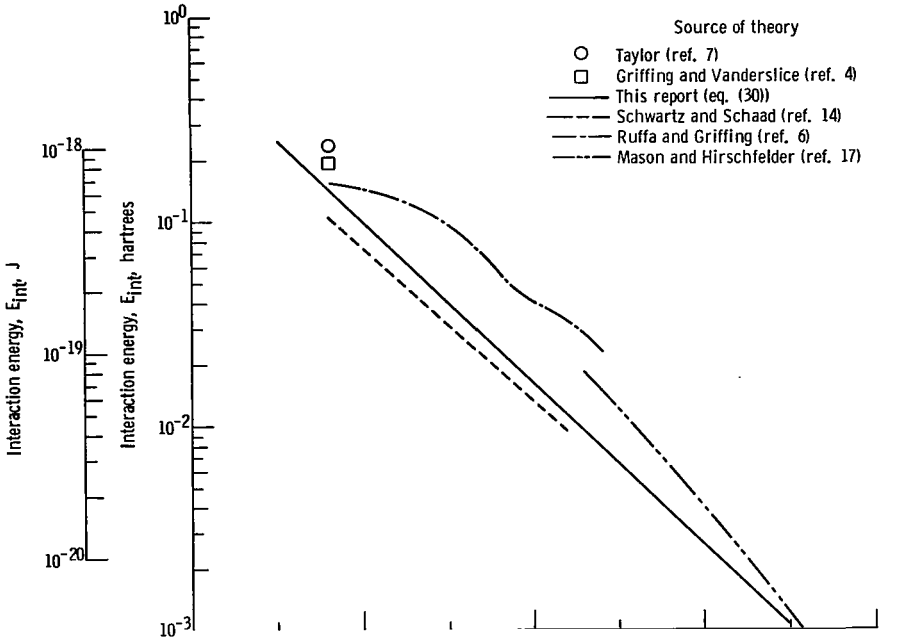
Energy and interaction energy of H_2 - H_2 were calculated from equations (29) and (30), respectively, and are given in table II for nine nuclear configurations and four intermolecular distances. For a given intermolecular distance, the linear configurations

TABLE II. - ENERGY AND ELECTRIC DIPOLE MOMENT FOR TWO HYDROGEN MOLECULES

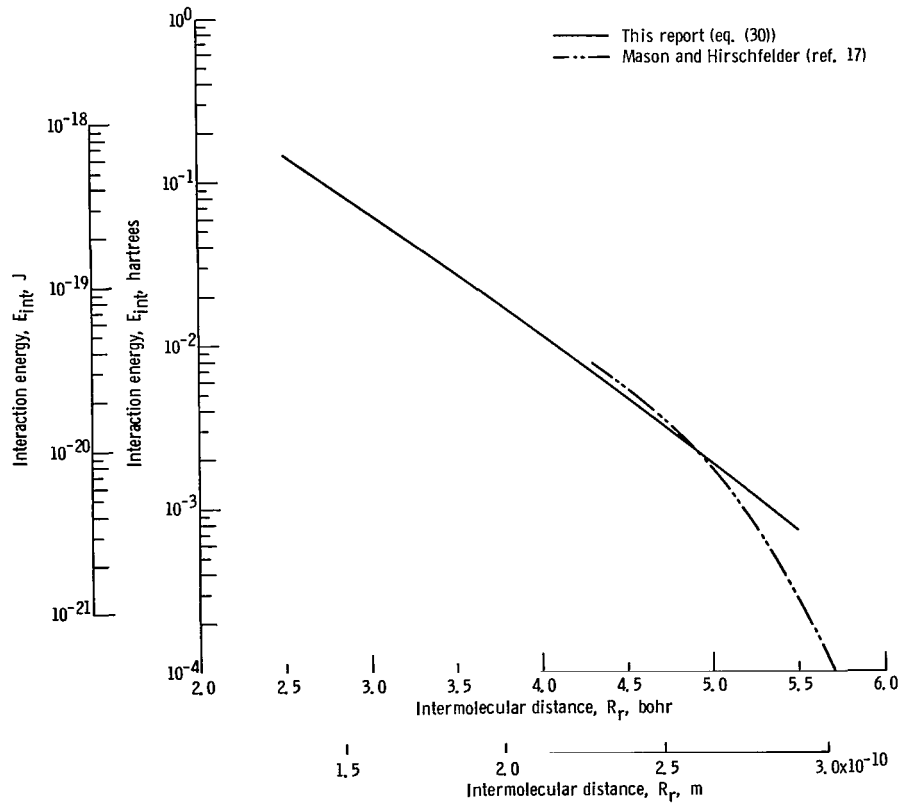
Intermolecular distance, R_r		Configuration[a]	Energy, E		Interaction energy, E_{int}		z-component of electric dipole moment[b]	
bohrs	m		hartree	J	hartree	J	at. units	C-m
2.5	1.3229×10^{-10}	A	-2.04492	-8.9147×10^{-18}	0.25066	1.0927×10^{-18}	0	0
		B	-2.03489	-8.8710	.26078	1.1369	.034890	2.958×10^{-31}
		C	-2.15035	-9.3743	.14523	.6331	-.347786	-2.949×10^{-30}
		D	-2.15018	-9.3736	.14549	.6343	-.343797	-2.915×10^{-30}
		E	-2.14658	-9.3579	.14909	.6499	-.384906	-3.263×10^{-30}
		F	-2.18153	-9.5102	.11406	.4972	0	0
		G	-2.18060	-9.5062	.11506	.5016	.004599	3.899×10^{-32}
		H	-2.18434	-9.5225	.11124	.4849	0	0
		I	-2.19410	-9.5650	.10157	.4428	.003720	3.154×10^{-32}
3.5	1.8521×10^{-10}	A	-2.25667	-9.8378×10^{-18}	0.03891	0.1696×10^{-18}	0	0
		B	-2.25540	-9.8323	.04026	.1755	.010739	9.104×10^{-32}
		C	-2.26824	-9.8882	.02734	.1192	-.097871	-8.297×10^{-31}
		D	-2.26800	-9.8872	.02766	.1206	-.097330	-8.251×10^{-31}
		E	-2.26735	-9.8844	.02832	.1235	-.109437	-9.278×10^{-31}
		F	-2.27440	-9.9151	.02118	.0923	0	0
		G	-2.27412	-9.9139	.02155	.0939	.001596	1.353×10^{-32}
		H	-2.27456	-9.9158	.02102	.0916	0	0
		I	-2.27706	-9.9267	.01861	.0811	.001287	1.091×10^{-32}
4.5	2.3813×10^{-10}	A	-2.28895	-9.9785×10^{-18}	0.00663	0.0289×10^{-18}	0	0
		B	-2.28874	-9.9776	.00692	.0302	.002468	2.092×10^{-32}
		C	-2.29084	-9.9868	.00475	.0207	-.024428	-2.071×10^{-31}
		D	-2.29082	-9.9867	.00485	.0211	-.024457	-2.073×10^{-31}
		E	-2.29070	-9.9861	.00497	.0217	-.027478	-2.330×10^{-31}
		F	-2.29194	-9.9916	.00364	.0159	0	0
		G	-2.29193	-9.9915	.00374	.0163	.000457	3.87×10^{-33}
		H	-2.29193	-9.9915	.00365	.0159	0	0
		I	-2.29257	-9.9943	.00310	.0135	.000357	3.03×10^{-33}
5.5	2.9104×10^{-10}	A	-2.29453	-10.0028×10^{-18}	0.00105	0.0046×10^{-18}	0	0
		B	-2.29456	-10.0030	.00111	.0048	.000498	4.22×10^{-33}
		C	-2.29484	-10.0042	.00074	.0032	-.005873	-4.979×10^{-32}
		D	-2.29490	-10.0045	.00076	.0033	-.005938	-5.034×10^{-32}
		E	-2.29488	-10.0044	.00078	.0034	-.006616	-5.609×10^{-32}
		F	-2.29500	-10.0049	.00058	.0025	0	0
		G	-2.29506	-10.0052	.00060	.0026	.000111	9.4×10^{-34}
		H	-2.29499	-10.0048	.00059	.0026	0	0
		I	-2.29519	-10.0057	.00048	.0021	.000084	7.1×10^{-34}

[a]See fig. 1.

[b]See fig. 1(a) for coordinates. Other components of the electric dipole moment are zero by symmetry.

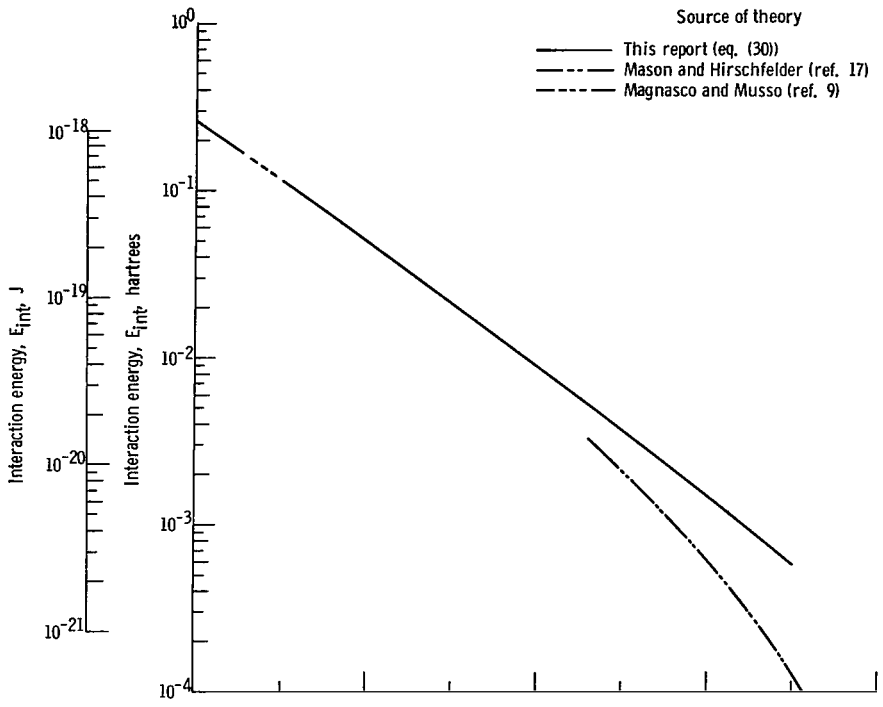


(a) Linear configuration A (see fig. 1(a)).

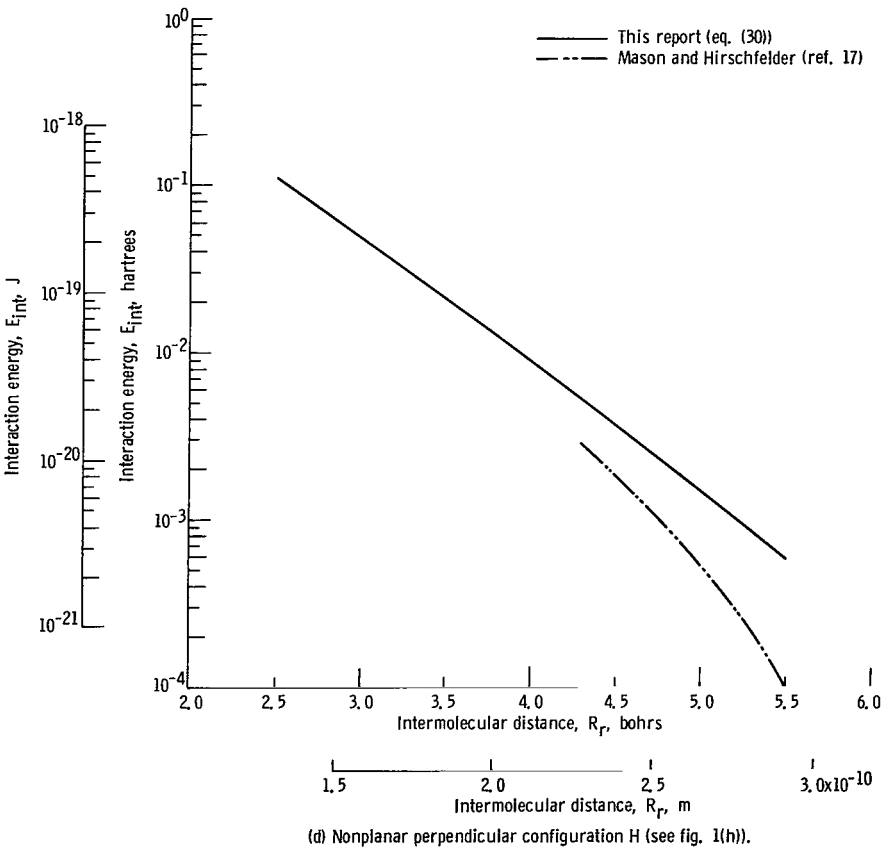


(b) Planar perpendicular configuration C (see fig. 1(c)).

Figure 3. - Interaction energy for four configurations of two hydrogen molecules, each configuration having equilibrium internuclear distances in both molecules.



(c) Quadrilateral configuration F (see fig. 1(f)). The curves for this report and from reference 9 coincide from R_r = 2.5 to 4.2478 bohrs.



(d) Nonplanar perpendicular configuration H (see fig. 1(h)).

Figure 3. - Concluded.

had the highest interaction energies, followed by the planar perpendicular configurations. The quadrilateral and nonplanar perpendicular configurations had the lowest interaction energies. It is not safe to draw any conclusions about the change in interaction energy between equilibrium and nonequilibrium configurations because the experimental equilibrium internuclear distance was used in this report rather than Weinbaum's value (ref. 25 and table I). Values of interaction energy in table II are plotted in figure 3 for the four equilibrium configurations. The interaction energies varied approximately exponentially with intermolecular distance.

H_2 - H_2 Average Interaction Energy

The average interaction energy of H_2 - H_2 was calculated from equation (31) for four intermolecular distances. Results are given in table III and are plotted in figure 4.

TABLE III. - AVERAGE INTERACTION ENERGY FOR TWO HYDROGEN MOLECULES WITH EQUILIBRIUM INTERNUCLEAR DISTANCES[a]

Intermolecular distance, R_r		Average interaction energy, $\overline{E}_{int}$	
bohrs	m	hartrees	J
2.5	1.3229×10^{-10}	0.14246	6.210×10^{-19}
3.5	1.8521	.02585	1.127
4.5	2.3813	.00447	.195
5.5	2.9104	.00071	.031

[a]Equilibrium internuclear distances of both molecules were 1.401446 bohrs (7.4160×10^{-11} m) (ref. 26).

H_2 - H_2 Electric Dipole Moment and Its Derivatives

The electric dipole moment of H_2 - H_2 was calculated from equation (39) for the nine configurations in figure 1 and four intermolecular distances. The x and y components were all essentially zero, as required by symmetry. The z component is given in table II. The planar perpendicular configurations had the largest magnitude of dipole

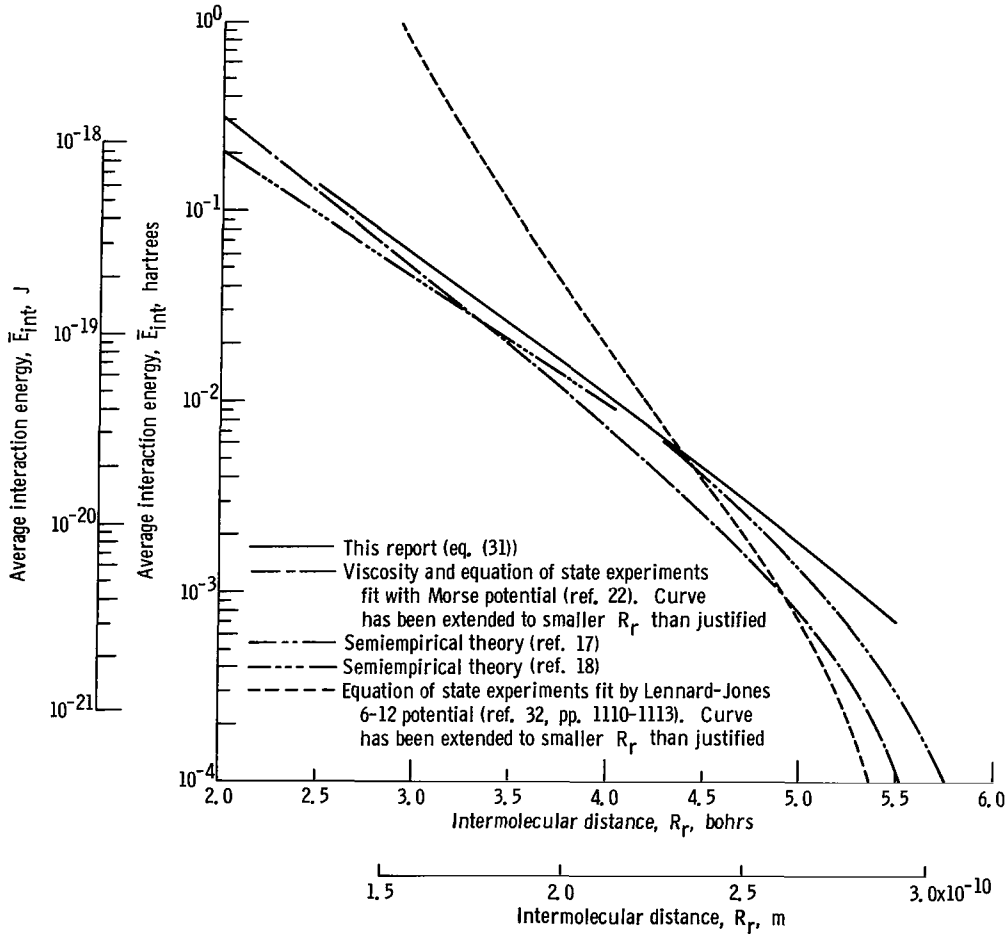


Figure 4. - Average interaction energy for two hydrogen molecules. The curve labelled "This report" was obtained by averaging interaction energies for the nine equally probable orientations given in figure 2.

moment because of their high degree of asymmetry. Equilibrium configurations A, F, and H had zero dipole moment by symmetry. The z component of dipole moment of equilibrium configuration C is plotted in figure 5. It varies approximately exponentially with intermolecular distance. The derivatives of the dipole moment with respect to internuclear distances were calculated from the dipole moments of the nine configurations (see table II) and are shown in figure 6.

Comparison of H_2 - H_2 Results with Other Investigators

Interaction energy. - Comparisons of E_{int} from equation (30) with ab initio results of other investigators are given in figure 3 for four H_2 - H_2 configurations with equilibrium internuclear distances in both molecules.

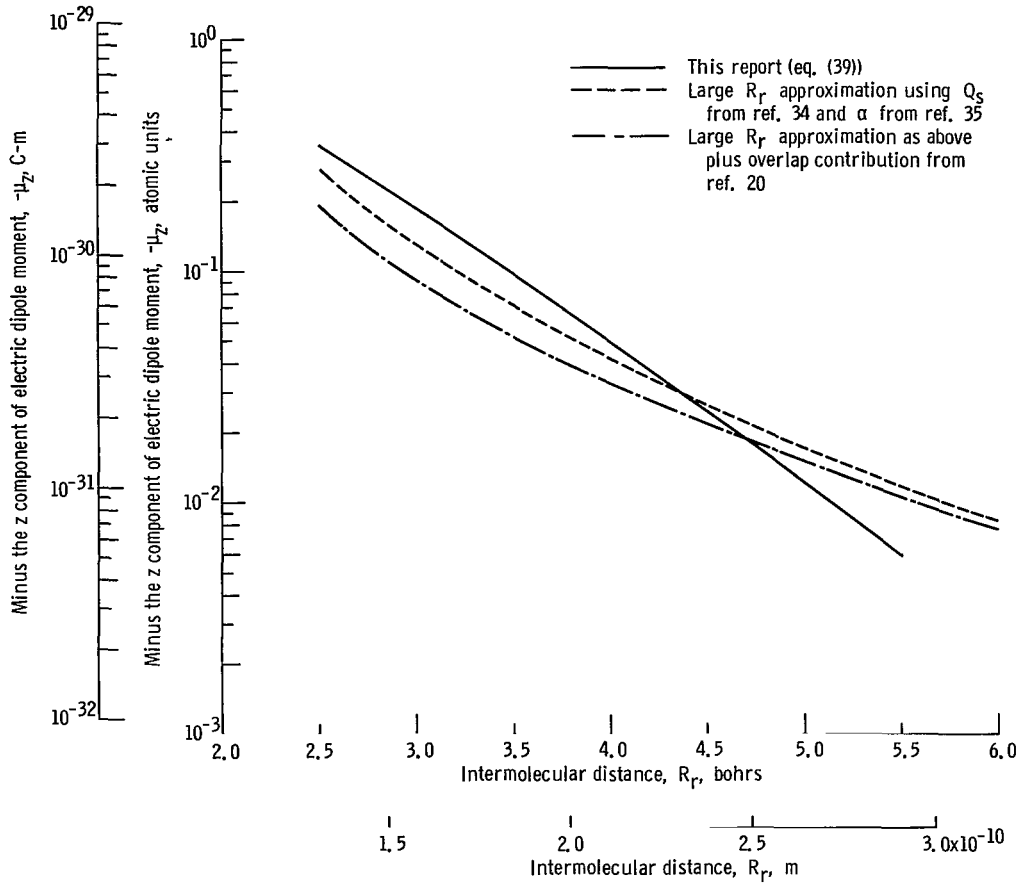


Figure 5. - z component of electric dipole moment for planar perpendicular configuration C (see fig. 1(c)) of two hydrogen molecules. Coordinates are shown in figure 1(a).

Figure 3(a) is for the linear configuration. The interaction energies of Griffing and Vanderslice (ref. 4) and Ruffa and Griffing (ref. 6) are high, possibly because of inaccurate molecular integrals. The energy of Taylor (ref. 7) is also high, possibly because he set all the orbital exponents equal to one. The energies of Schwartz and Schaad (ref. 14) are lower than our energies. The variation principle states that E is an upper limit, but gives no information on E_{int}. Consequently, this principle cannot be used to show that Schwartz and Schaad's E_{int} is best. However, since they used 24 orbitals compared with four in this report, their E_{int} is probably best for the range of R_r they covered. The theory of Mason and Hirschfelder (ref. 17) is believed best at large R_r but is not accurate at small R_r because it is principally a perturbation calculation. Its superiority at large R_r is due to its accurate semiempirical treatment of dispersion energy.

Figures 3(b) to (d) are for the planar perpendicular, quadrilateral, and nonplanar perpendicular configurations, respectively. The E_{int} of Mason and Hirschfelder

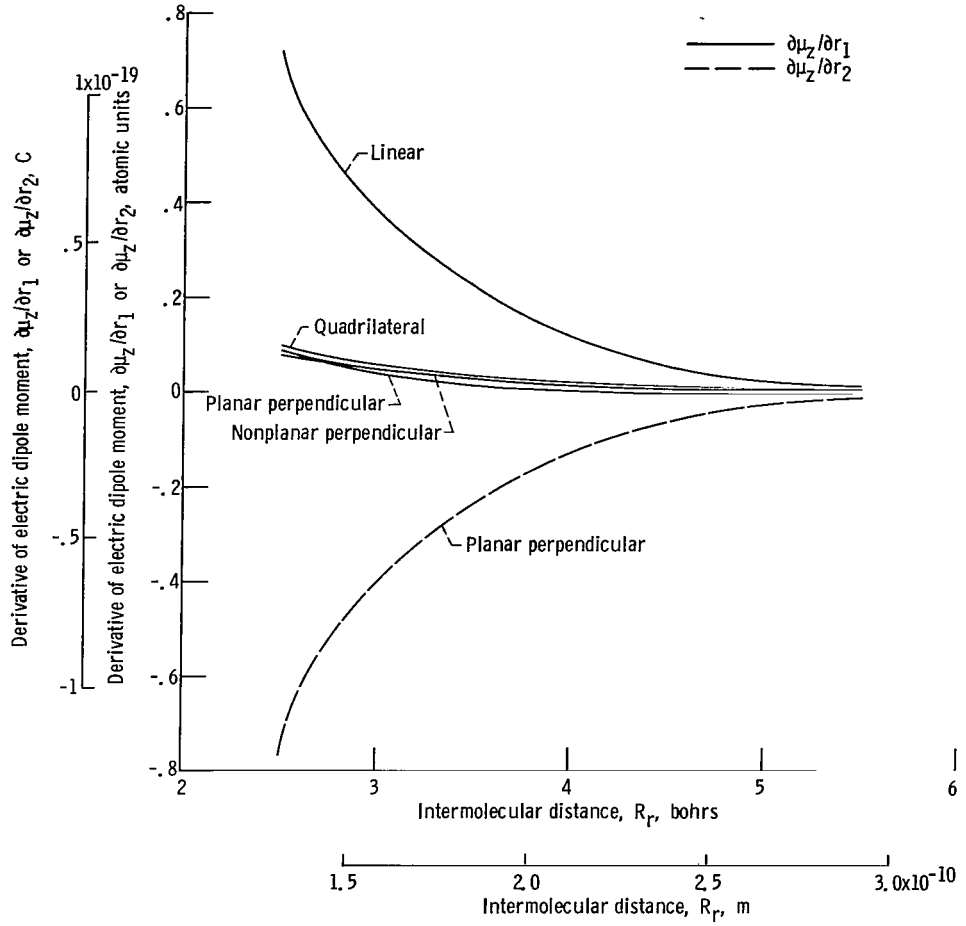


Figure 6. - Derivatives of electric dipole moment with respect to internuclear distance for various configurations of two hydrogen molecules. Internuclear distances r_1 and r_2 are the distances between the nuclei of molecules 1 and 2, respectively (see fig. 1).

(ref. 17) are believed best at large R_r. For the quadrilateral configuration there is no discernible difference between Magnasco and Musso's E_{int} (ref. 9) and our E_{int}.

Average interaction energy. - Comparison of $\overline{E}_{int}$ from equation (31) with results of other investigators are given in figure 4 for H_2 - H_2 with equilibrium internuclear distances in both molecules. The Lennard-Jones 6-12 potential (ref. 32) was fitted to data from moderate temperature equation-of-state experiments and hence is not accurate at small R_r. The Morse potential (ref. 22) was fitted to moderate temperature equation-of-state and viscosity data and also to viscosity data up to 2340 K (ref. 21); therefore, it should be valid down to R_r = 4.0 bohrs (2.1×10^{-10} m). However, it is obviously wrong for small enough R_r because it does not approach infinity as R_r approaches zero. Thus its agreement with equation (31) for $2.5 \leq R_r \leq 4$ bohrs ($0.13 \leq R_r \leq 0.21$ nm) is surprising. Two semiempirical theories (refs. 17 and 18) are included in figure 4 for reference only. I believe the excessive values of $\overline{E}_{int}$ from equation (31) for large R_r

are due to insufficient allowance for electron correlation in the wave function. This causes the magnitude of the dispersion energy (which is a negative quantity) to be low.

Electric dipole moment. - Comparisons of μ_z from equation (39) with results of other investigators are given in figure 5 for the planar perpendicular configuration. The large R_r approximation was obtained by considering the polarization of each H_2 molecule by the electric quadrupole of the other. The scalar quadrupole moment Q_s and polarizability α of H_2 were obtained from Kolos and Wolniewicz (refs. 34 and 35) and inspire confidence. The resulting μ_z varies as $1/R_r^4$ as shown and is correct without much doubt for large enough R_r. A curve is also given in figure 5 for the large R_r approximation plus a semiempirical overlap contribution (ref. 20). The overlap contribution is not large, so the trend is essentially the same as for the large R_r approximation alone. Equation (39) does not follow either dashed curve for $R_r > 4.5$ bohrs (0.24 nm) and, in fact, is even curved the wrong way. I believe this difficulty is due to the model used: at large R_r it essentially describes two covalent-ionic valence-bond H_2 molecules, which have no polarizability perpendicular to their axes and probably have incorrect quadrupole moments. (The quadrupole moment is very sensitive to the electronic charge distribution.) Consequently, the orthogonalized valence-bond theory used in this report does not give reliable μ_z for $R_r > 4.5$ bohrs (0.24 nm) despite the inclusion of singly and doubly polar structures.

CONCLUDING REMARKS

Full valence-bond ab initio calculations of H_2 - H_2 interaction energy and electric dipole moment were carried out with accurate values for all molecular integrals. Linear, planar perpendicular, quadrilateral, and nonplanar perpendicular configurations were included with intermolecular distances from 2.5 to 5.5 bohr (0.13 to 0.29 nm). A weighted average of the interaction energies of the four equilibrium configurations was then taken.

The interaction energies obtained appear to be valid for intermolecular distances less than 4.5 bohr (0.24 nm) but are too large at appreciably greater intermolecular distances because of insufficient allowance for electron correlation in the wave function.

Fisher (ref. 22) has fitted a Morse potential to viscosity and equation-of-state data, and this potential should be valid down to intermolecular distances of 4.0 bohrs (0.21 nm), based on the temperatures at which the data were taken. The calculations in this report show that this Morse potential is also a good approximation for intermolecular distances between 2.5 and 4.0 bohrs (0.13 and 0.21 nm). Consequently, this Morse potential is useful for practical applications for all R_r greater than 2.5 bohrs (0.13 nm).

The electric dipole moments obtained by the full valence-bond calculation appear to

be approximately correct for intermolecular distances up to 4.5 bohrs (0.24 nm). For appreciably larger distances they are too small due to limitations of the model. The derivatives of the dipole moment with respect to the internuclear distances of the H_2 molecules were also obtained. These are necessary to calculate pressure-induced vibrational absorption coefficients.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, July 23, 1969,
122-28.

APPENDIX A

SYMBOLS

A	definite integral involving exponential
$(ab\overline{cd})$	shorthand notation for antisymmetrized product of orthogonalized spin-orbitals
$\underline{C}$	column vector of coefficients of ψ_j
$\underline{C'}$	column vector of coefficients of φ_i
C_{pj}	j^{th} Cartesian coordinate of proton p
$\overline{C}_{ppj}$	j^{th} Cartesian coordinate of center of atomic charge p
$\overline{C}_{pqj}$	j^{th} Cartesian coordinate of center of overlap charge pq
C'_r	element of $\underline{C'}$
$\underline{d}$	matrix of overlap eigenvalues
$\underline{d}^{-1/2}$	inverse square root of $\underline{d}$
$d_{ii}^{-1/2}$	diagonal element of $\underline{d}^{-1/2}$
E	electronic and nuclear repulsion energy of complex
E_e	electronic energy
E_{int}	interaction energy
$\overline{E}_{int}$	average interaction energy
E_m	electronic and nuclear repulsion energy of diatomic molecule
$\overline{F}_{ij}$	one-electron integral of orthogonalized orbitals
$\overline{G}_{ijk\ell}$	two-electron integral of orthogonalized orbitals
G_k^i	definite integral involving exponential and Legendre function of first kind
G_{mnop}	two-electron integral of 1s orbitals
$\underline{H}$	Hamiltonian matrix with basis functions ψ_j
$\hat{H}$	Hamiltonian operator for electrons
H_k	definite integral involving exponential and Legendre functions of first and second kinds
H_{nk}	element of $\underline{H}$
$\underline{H_\varphi}$	Hamiltonian matrix with basis functions φ_i
$(H_\varphi)_{ij}$	element of $\underline{H_\varphi}$
$\hbar$	Planck constant divided by 2π
J	center of orbital χ_j
K	center of orbital χ_k
K_k^i	definite integral involving exponential and Legendre function of first kind
$K_{k\ell}$	kinetic energy integral
L_{jkp}	nuclear attraction integral
L_k^i	definite integral involving exponential and Legendre function of second kind
M	center of orbital χ_m

$\underline{M_\chi^{-1/2}}$	Löwdin transformation matrix
$\left(M_\chi^{-1/2}\right)_{ki}$	element of $\underline{M_\chi^{-1/2}}$
N	center of orbital χ_n
$n_{rs}^{m\alpha n\alpha}$	coefficients of spin-orbital products with two α spins
$n_{rs}^{m\beta n\beta}$	coefficients of spin-orbital products with two β spins
P	center of proton p
$\underline{\mathscr{P}}$	matrix of $\mathscr{P}_{pq}$
P_k	Legendre function of first kind
P'_{mn}	electron population in the orbital density $\chi'_m\chi'_n$ irrespective of spin state
P_{pq}	electron population in the orbital density $\chi_p\chi_q$ irrespective of spin state
$\mathscr{P}_{pq}$	normalized one-electron population
p_k^j	constants in Legendre function of first kind
Q_k	Legendre function of second kind
Q_s	scalar quadrupole moment
$\check{q}$	$(\zeta_p - \zeta_q)R_{pq}/2$ (subscripts vary)
$\hat{q}$	$(\zeta_m - \zeta_o)R_{mo}$
$\overline{q}$	$(3\zeta_m - \zeta_p)R_{mp}/2$
R_{pq}	distance between points p and q
R_r	intermolecular distance (see fig. 1)
r, r_i	internuclear distance of diatomic molecule i
$\hat{r}$	$(\zeta_m + \zeta_o)R_{mo}$
$\overline{r}$	$(3\zeta_m + \zeta_p)R_{mp}/2$
r_{ij}	distance between electron or proton i and electron j
$\underline{S}$	matrix of S_{pq}
S_{pq}	overlap integral for χ_p and χ_q
T	definite integral involving exponential
$\underline{U}$	unitary matrix
$\underline{\tilde{U}}$	tranpose of $\underline{U}$
$U_{mn}(2)$	electrostatic potential at electron 2 due to the bicentric charge distribution $\chi_m(1)\chi_n(1)$
u	variable of integration
$\underline{V}$	matrix relating $\underline{\psi}$ and $\underline{\varphi}$
$\underline{\tilde{V}}$	transpose of $\underline{V}$
v_i	volume in configuration space for electron i
w, w_{pq}	$(\zeta_p + \zeta_q)R_{pq}/2$
X_k, Z_k	x and z coordinates of point K in units of $R_{pj}/2$
x, y, z	Cartesian coordinates
α	polarizability
$\alpha(i)$	spin eigenfunction of electron i with component of spin angular momentum along the axis of quantization equal to $\hbar/2$
$\beta(i)$	spin eigenfunction of electron i with component of spin angular momentum along the axis of quantization equal to $-\hbar/2$

Δ_{pq} displacement of overlap charge center for p-q geometric center, measured in direction from p towards q and expressed in units of R_{pq}

ζ orbital exponent

ζ_p orbital exponent of χ_p

θ, μ, ν spheroidal coordinates

λ $-1/\mu$

μ_k μ of point K

μ_∞ finite upper limit for μ integration

$\mu(<)$ smaller of μ_1 and μ_2

$\mu(>)$ larger of μ_1 and μ_2

τ volume in configuration and spin space of four electrons

$\underline{\varphi}$ row vector with elements φ_i

φ_i antisymmetrized product of orthogonalized spin-orbitals

$\underline{\chi}$ row vector with elements χ_p

$\underline{\chi'}$ row vector with elements χ'_p

$\chi_p(i)$ 1s orbital of electron i centered on proton p

$\chi'_p(i)$ orthogonalized orbital of electron i

Ψ wave function of system

$\underline{\psi}$ row vector with elements ψ_j

ψ_j formal orthogonalized valence-bond structure

APPENDIX B

EVALUATION OF KINETIC ENERGY INTEGRALS

Herein methods are given for evaluating kinetic energy integrals involving 1s atomic orbitals (eq. (1)) with equal or unequal orbital exponents. These integrals all have the form

$$K_{k\ell} \equiv \int \chi_k(1)\left(-\frac{1}{2}\nabla_1^2\right)\chi_\ell(1)dv_1 \tag{B1}$$

Equal Orbital Exponents

Analytic expressions for $K_{k\ell}$ for the two cases $k = \ell$ and $k \neq \ell$ have been given in reference 3 (p. 50) (but a typographical error must be corrected in the $k \neq \ell$ case).

Unequal Orbital Exponents

If $k \neq \ell$ and the orbital exponents are unequal, the integral in equation (B1) may be found analytically by the methods in reference 3.

$$K_{k\ell} = -\frac{1}{8}R_{k\ell}^3\zeta_\ell\sqrt{\zeta_k^3\zeta_\ell^3}\left\{\zeta_\ell\frac{e^{\check{q}}-e^{-\check{q}}}{\check{q}}\frac{2}{w_{k\ell}^2}\left(1+w_{k\ell}+\frac{1}{2}w_{k\ell}^2\right)\right.$$

$$+\zeta_\ell\left[e^{-\check{q}}\left(\frac{1}{\check{q}}+\frac{2}{\check{q}^2}+\frac{2}{\check{q}^3}\right)+e^{\check{q}}\left(-\frac{1}{\check{q}}+\frac{2}{\check{q}^2}-\frac{2}{\check{q}^3}\right)\right]-\frac{4}{R_{k\ell}}\frac{e^{\check{q}}-e^{-\check{q}}}{\check{q}}\frac{1+w_{k\ell}}{w_{k\ell}}$$

$$\left.+\frac{4}{R_{k\ell}}\left[e^{-\check{q}}\left(\frac{1}{\check{q}}+\frac{1}{\check{q}^2}\right)+e^{\check{q}}\left(\frac{1}{\check{q}}-\frac{1}{\check{q}^2}\right)\right]\right\}\frac{e^{-w_{k\ell}}}{w_{k\ell}} \tag{B2}$$

where $w_{k\ell}$ is given by equation (3) and where

$$\breve{q} \equiv \frac{\left(\zeta_k - \zeta_l\right) R_{kl}}{2} \tag{B3}$$

All K_{kl} were evaluated to within ±1 in the sixth significant digit.

APPENDIX C

EVALUATION OF NUCLEAR ATTRACTION INTEGRALS

Methods for evaluating nuclear attraction integrals involving 1s atomic orbitals (eq. (1)) with equal or unequal orbital exponents are given herein. These integrals all have the form

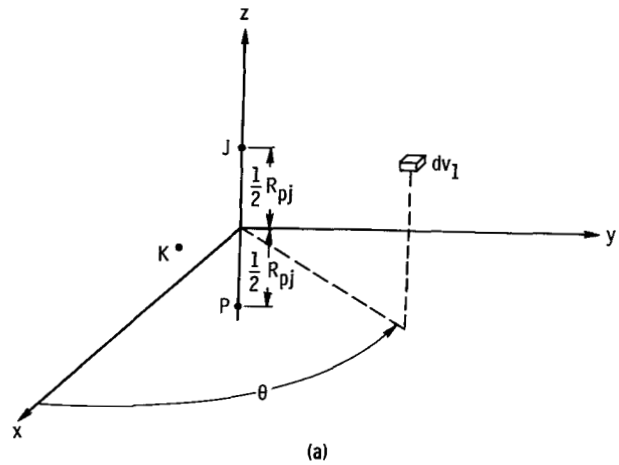
$$L_{jkp} \equiv \int \chi_j(1)\chi_k(1)\left(\frac{-1}{r_{p1}}\right) dv_1 \qquad \text{(C1)}$$

where r_{p1} is the distance from proton p to electron 1.

Equal Orbital Exponents

If all three subscripts of L_{jkp} are equal or if only two of them are equal, analytic expressions for L_{jkp} are given in reference 3 (p. 50). If all subscripts are different, numerical integration is required and is described in the following paragraphs.

Numerical integration of three-center integrals is best done in spheroidal coordinates (ref. 3). First, however, a set of Cartesian coordinates is selected with the origin half way between P and J and with the z axis in the direction from P to J.



(a)

The x axis is chosen so K is in the x-z plane with x_k zero or positive. The three spheroidal coordinates θ, μ, and ν can now be defined. The azimuthal angle measured around the z axis as shown is called θ. The other two coordinates are

$$\mu \equiv \frac{r_{p1} + r_{j1}}{R_{pj}} \tag{C2}$$

$$\nu \equiv \frac{r_{p1} - r_{j1}}{R_{pj}} \tag{C3}$$

where r_{p1} is the distance from P to dv_1, and r_{j1} is the distance from J to dv_1. Surfaces of constant μ are ellipsoids of revolution about the z axis with foci at P and J. Surfaces of constant ν are hyperboloids of revolution about the z axis with foci at P and J except for $\nu = 0$, which is the x-y plane.

In these coordinates, equation (C1) becomes

$$L_{jkp} = -\frac{R_{pj}^2}{2\pi}\sqrt{\zeta_j^3\zeta_k^3}\int_1^\infty\int_{-1}^1 (\mu - \nu)e^{-\zeta_j\frac{R_{pj}}{2}(\mu-\nu)}\int_0^\pi \exp\left[-\zeta_k\frac{R_{pj}}{2}\left(X_k^2 + Z_k^2 - 1 + \mu^2 + \nu^2 - 2\mu\nu Z_k - 2X_k\sqrt{\mu^2-1}\sqrt{1-\nu^2}\cos\theta\right)^{1/2}\right]d\theta d\nu d\mu \tag{C4}$$

where X_k and Z_k are x_k and z_k, respectively, in units of $R_{pj}/2$. The θ integration was done by a single Gaussian quadrature. The ν integration was done by using two Gaussian quadratures: one from -1 to ν_k and one from ν_k to 1. The μ integration was also split into two parts. Integration from 1 to μ_k was done by Gaussian quadrature. From μ_k to an upper limit μ_∞ the integration was done by transforming the integral so it was with respect to a variable $\lambda = -1/\mu$ and applying Gaussian quadrature. (The author is indebted to Professor V. Magnasco, Universita di Genova, Genoa, for this idea.) In each case an appropriate finite μ_∞ had to be calculated to replace ∞ as the upper limit in the μ integration.

Use of the coordinate system shown was superior to use of the coordinate system in reference 36 because it gave better accuracy for the same number of integration points for cases where J, K, and P were in line or almost in line. This was apparently because the integrand in equation (C4) is everywhere finite, which is not the case for the equation in different coordinates in reference 36.

Unequal Orbital Exponents

If $j = k \neq p$, the only two orbital exponents that occur in the integral are identical. However, if $p = j \neq k$ or $p = k \neq j$, the unequal orbital exponents result in new expressions for L_{jkp}. For the case $p = k \neq j$

$$L_{jkp} = -\frac{1}{2} R_{jk}^2 \sqrt{\zeta_j^3 \zeta_k^3} \left[\frac{e^{\check{q}} - e^{-\check{q}}}{\check{q}} \frac{1 + w_{jk}}{w_{jk}} - e^{-\check{q}} \left(\frac{1}{\check{q}} + \frac{1}{\check{q}^2} \right) - e^{\check{q}} \left(\frac{1}{\check{q}} - \frac{1}{\check{q}^2} \right) \right] \frac{e^{-w_{jk}}}{w_{jk}} \tag{C5}$$

where the methods of reference 3 were used and where

$$\check{q} \equiv \frac{(\zeta_j - \zeta_k) R_{jk}}{2} \tag{C6}$$

For the case where none of the subscripts of L_{jkp} are equal, equation (C4) is applicable.

All L_{jkp} were evaluated to within ±3 in the sixth significant digit.

APPENDIX D

EVALUATION OF TWO-ELECTRON INTEGRALS

Methods are given for evaluating two-electron integrals involving 1s atomic orbitals (eq. (1)) with equal or unequal orbital exponents. These integrals all have the form

$$G_{mnop} = \iint \chi_m(1)\chi_n(1)\chi_o(2)\chi_p(2) \frac{1}{r_{12}} dv_1 dv_2 \tag{D1}$$

where r_{12} is the distance between the two electrons.

Equal Orbital Exponents

One-center integral. - An expression for G_{mnop} when all the subscripts are equal is given in reference 3 (p. 65).

Two-center Coulomb integral. - If $m = n$ and $o = p$, an expression for G_{mnop} is given in reference 3 (p. 50).

Two-center exchange integral. - If $m = o$ and $n = p$, an expression for G_{mnop} is given in reference 3 (p. 50), but it requires correction of a typographical error. The expression involves the integral logarithm, which was evaluated using the program of Dellepiane, Ferro, and Magnasco (ref. 33).

Two-center hybrid integral. - An expression for G_{mnop} if three of the subscripts are identical is given in reference 3 (p. 65).

Three-center Coulomb integral. - If $m = n \neq o \neq p$ or $m \neq n \neq o = p$, the integral must be integrated numerically. The method of Magnasco and Dellepiane (ref. 36) was used except that on the outer μ integration range the μ integral was transformed so that it was with respect to a variable $\lambda = -1/\mu$ and Gaussian quadrature was applied.

Three-center exchange integral. - If one of the first two subscripts equalled one of the last two subscripts of G_{mnop}, the integral was integrated numerically by the method of Magnasco and Dellepiane (ref. 37) except that on the outer μ integration range the method of the preceding paragraph was used.

Four-center integral. - For cases where all the subscripts of G_{mnop} were different, an evaluation method has been given by Magnasco and Dellepiane (ref. 37). This method was used with three modifications to improve the accuracy: (1) on the outer μ integration range the μ integral was transformed so it was with respect to a variable $\lambda = -1/\mu$, and Gaussian quadrature was applied; (2) in some cases three μ integration

ranges were used instead of two; and (3) in some cases three ν integration ranges were used instead of two.

Unequal Orbital Exponents

Two-center Coulomb integral. - Here m = n and o = p. Using the methods in reference 3 gives

$$G_{mnop} = \frac{1}{2}\zeta_o^3 R_{mo}^2 \left\{ \frac{2}{\zeta_o^3 R_{mo}^3} - 2e^{-2\zeta_o R_{mo}} \left(\frac{1}{\zeta_o^3 R_{mo}^3} + \frac{1}{\zeta_o^2 R_{mo}^2} \right) - \frac{e^{\hat{q}} - e^{-\hat{q}}}{\hat{q}} \frac{e^{-\hat{r}}}{\hat{r}^2} (1 + \hat{r}) \right.$$

$$- \left[e^{-\hat{q}} \left(\frac{1}{\hat{q}} + \frac{1}{\hat{q}^2} \right) + e^{\hat{q}} \left(\frac{1}{\hat{q}} - \frac{1}{\hat{q}^2} \right) \right] \frac{e^{-\hat{r}}}{\hat{r}} - \zeta_m R_{mo} \frac{e^{\hat{q}} - e^{-\hat{q}}}{\hat{q}} \frac{e^{-\hat{r}}}{\hat{r}^3} \left(1 + \hat{r} + \frac{\hat{r}^2}{2} \right)$$

$$\left. - \frac{1}{2}\zeta_m R_{mo} \left[e^{-\hat{q}} \left(\frac{1}{\hat{q}} + \frac{2}{\hat{q}^2} + \frac{2}{\hat{q}^3} \right) + e^{\hat{q}} \left(-\frac{1}{\hat{q}} + \frac{2}{\hat{q}^2} - \frac{2}{\hat{q}^3} \right) \right] \frac{e^{-\hat{r}}}{\hat{r}} \right\} \tag{D2}$$

where

$$\hat{r} \equiv (\zeta_m + \zeta_o) R_{mo} \tag{D3}$$

and

$$\hat{q} \equiv (\zeta_m - \zeta_o) R_{mo} \tag{D4}$$

Two-center exchange integral. - Here m = o and n = p. This can be expressed as an infinite series. Spheroidal coordinates were used for both electrons. The quantity $1/r_{12}$ was expanded in the Newmann expansion (ref. 3, p. 266) with the result

$$G_{mnop} = \frac{1}{8} R_{mn}^5 \zeta_m^3 \zeta_n^3 \sum_{k=0}^{\infty} (2k + 1) \left[G_k^0(\check{q})^2 H_k(2, 2, w_{mn}) \right.$$

$$\left. - 2G_k^0(\check{q}) G_k^2(\check{q}) H_k(0, 2, w_{mn}) + G_k^2(\check{q})^2 H_k(0, 0, w_{mn}) \right] \tag{D5}$$

where w_{mn} is given by equation (3) and

$$\check{q} \equiv \frac{\zeta_m - \zeta_n}{2} R_{mn} \tag{D6}$$

$$G_k^i(\check{q}) \equiv \int_{-1}^{1} \nu^i e^{-\check{q}\nu} P_k(\nu) d\nu \tag{D7}$$

$$H_k(i,j,w) \equiv \int_1^\infty \int_1^\infty P_k\left[\mu(<)\right] Q_k\left[\mu(>)\right] \mu_1^i \mu_2^j e^{-w(\mu_1 + \mu_2)} d\mu_1 d\mu_2 \tag{D8}$$

Here the P_k and Q_k are Legendre functions of the first and second kinds, respectively, $\mu(<)$ is the smaller of μ_1 and μ_2, and $\mu(>)$ is the larger of μ_1 and μ_2. The G_k^i integrals were evaluated by Rosen (ref. 38). The H_k integrals were evaluated by James and Coolidge (ref. 39) and Rosen (ref. 40).

Two-center hybrid integral. - Here, three of the subscripts are identical. This case may be integrated by methods in reference 3. If the first three subscripts are identical,

$$G_{mnop} = \frac{1}{2} R_{mp}^2 \sqrt{\zeta_m^3 \zeta_p^3} \left\{ \frac{e^{-w_{mp}}}{w_{mp}} \left[\frac{e^{\check{q}} - e^{-\check{q}}}{\check{q}} \frac{1 + w_{mp}}{w_{mp}} + e^{-\check{q}} \left(\frac{1}{\check{q}} + \frac{1}{\check{q}^2} \right) + e^{\check{q}} \left(\frac{1}{\check{q}} - \frac{1}{\check{q}^2} \right) \right] \right.$$

$$- \frac{e^{-\bar{r}}}{\bar{r}} \left[\frac{e^{\bar{q}} - e^{-\bar{q}}}{\bar{q}} \frac{1 + \bar{r}}{\bar{r}} + e^{-\bar{q}} \left(\frac{1}{\bar{q}} + \frac{1}{\bar{q}^2} \right) + e^{\bar{q}} \left(\frac{1}{\bar{q}} - \frac{1}{\bar{q}^2} \right) \right]$$

$$\left. - \frac{1}{2} \zeta_m R_{mp} \frac{e^{-\bar{r}}}{\bar{r}} \left[\frac{e^{\bar{q}} - e^{-\bar{q}}}{\bar{q}} \frac{2 + 2\bar{r} + \bar{r}^2}{\bar{r}^2} + e^{-\bar{q}} \left(\frac{1}{\bar{q}} + \frac{2}{\bar{q}^2} + \frac{2}{\bar{q}^3} \right) + e^{\bar{q}} \left(-\frac{1}{\bar{q}} + \frac{2}{\bar{q}^2} - \frac{2}{\bar{q}^3} \right) \right] \right\} \tag{D9}$$

where w_{mp} is given by equation (3) and

$$\check{q} \equiv \frac{\zeta_m - \zeta_p}{2} R_{mp} \tag{D10}$$

$$\overline{r} \equiv \frac{3\zeta_m + \zeta_p}{2} R_{mp} \tag{D11}$$

$$\overline{q} \equiv \frac{3\zeta_m - \zeta_p}{2} R_{mp} \tag{D12}$$

Three-center Coulomb integral. - Here, $m = n \neq o \neq p$ or $m \neq n \neq o = p$ in G_{mnop}. The method of evaluation was the same as for equal orbital exponents.

Three-center exchange and four-center integrals. - The methods of evaluating these integrals were the same as for equal orbital exponents with the following exception. The methods of Magnasco and Dellepiane (ref. 37) require evaluation of

$$U_{mn}(2) = \int \chi_m(1)\chi_n(1) \frac{1}{r_{12}} dv_1 \tag{D13}$$

as a step in their procedure, where $U_{mn}(2)$ is the electrostatic potential at electron 2 due to the bicentric charge distribution $\chi_m(1)\chi_n(1)$. They give an expression for $U_{mn}(2)$ if $\zeta_m = \zeta_n$, but not if $\zeta_m \neq \zeta_n$. A solution for $\zeta_m \neq \zeta_n$ will now be given.

An infinite series for $U_{mn}(2)$ with $\zeta_m \neq \zeta_n$ may be derived by using spheroidal coordinates for both electrons 1 and 2. These coordinates were the same as in appendix C except that M replaced P and N replaced J. The quantity $1/r_{12}$ was expressed as a Neumann expansion. The result is

$$U_{mn}(2) = \frac{1}{2} R_{mn}^2 \sqrt{\zeta_m^3 \zeta_n^3} \sum_{k=0}^{\infty} (2k+1) P_k(\nu_2) \Big\{ Q_k(\mu_2) \Big[G_k^0(\check{q}) K_k^2(w_{mn}, \mu_2) - G_k^2(\check{q}) K_k^0(w_{mn}, \mu_2) \Big] + P_k(\mu_2) \Big[G_k^0(\check{q}) L_k^2(w_{mn}, \mu_2) - G_k^2(\check{q}) L_k^0(w_{mn}, \mu_2) \Big] \Big\} \tag{D14}$$

where

$$K_k^i(w, \mu_2) \equiv \int_1^{\mu_2} e^{-w\mu_1} P_k(\mu_1) \mu_1^i d\mu_1 \tag{D15}$$

and

$$L_k^i(w,\mu_2) \equiv \int_{\mu_2}^{\infty} e^{-w\mu_1} Q_k(\mu_1)\mu_1^i d\mu_1 \tag{D16}$$

The integrals K_k^i may easily be evaluated explicitly. To do this, the Legendre function of the first kind may be expressed as

$$P_k(\mu) = \sum_{j=0}^{k} p_k^j \mu^j \tag{D17}$$

where the p_k^j are constants. Substituting equation (D17) into (D15) gives

$$K_k^i(w,\mu) = \sum_{j=0}^{k} p_k^j A(w,\mu,j+i) \tag{D18}$$

where

$$A(w,\mu,0) = \frac{1}{w}(-e^{-w\mu} + e^{-w}) \tag{D19}$$

and the recursion relation is

$$A(w,\mu,h) = \frac{1}{w}\left[-\mu^h e^{-w\mu} + e^{-w} + hA(w,\mu,h-1)\right] \tag{D20}$$

The integrals L_k^i are not so easy to evaluate to six significant digits. The Legendre function of the second kind may be expanded in a hypergeometric series

$$Q_k(\mu) = \frac{k!}{\mu^{k+1}(2k+1)!!}\left[1 + \frac{\left(\frac{k}{2}+1\right)\left(\frac{k}{2}+\frac{1}{2}\right)}{\left(k+\frac{3}{2}\right)\mu^2} + \frac{\left(\frac{k}{2}+1\right)\left(\frac{k}{2}+2\right)\left(\frac{k}{2}+\frac{1}{2}\right)\left(\frac{k}{2}+\frac{3}{2}\right)}{\left(k+\frac{3}{2}\right)\left(k+\frac{5}{2}\right)2\mu^4}\right.$$

$$\left. + \frac{\left(\frac{k}{2}+1\right)\left(\frac{k}{2}+2\right)\left(\frac{k}{2}+3\right)\left(\frac{k}{2}+\frac{1}{2}\right)\left(\frac{k}{2}+\frac{3}{2}\right)\left(\frac{k}{2}+\frac{5}{2}\right)}{\left(k+\frac{3}{2}\right)\left(k+\frac{5}{2}\right)\left(k+\frac{7}{2}\right)6\mu^6} + \cdots\right] \tag{D21}$$

which is abbreviated as

$$Q_k(\mu) = \frac{k!}{\mu^{k+1}\,(2k+1)!!} \sum_{j=0}^{\infty} \frac{\left(\frac{k}{2}+1\right)_j \left(\frac{k}{2}+\frac{1}{2}\right)_j}{\left(k+\frac{3}{2}\right)_j\, j!\, \mu^{2j}} \tag{D22}$$

Substituting equation (D22) into (D16) gives

$$L_k^i(w,\mu) = \frac{k!}{(2k+1)!!} \sum_{j=0}^{\infty} \frac{\left(\frac{k}{2}+1\right)_j \left(\frac{k}{2}+\frac{1}{2}\right)_j}{\left(k+\frac{3}{2}\right)_j\, j!}\, T(w,\mu,i-2j-k-1) \tag{D23}$$

where

$$T(w,\mu,h) \equiv \int_{\mu}^{\infty} e^{-wu} u^h du \tag{D24}$$

and h can be a positive or negative integer or zero. Equation (D24) was integrated analytically to get T in terms of exponentials and integral logarithms. If $\mu \geq 1.2$, equation (D23) gives six significant digits without too many terms. For $\mu \leq 1.2$, it is better to use

$$L_k^i(w,\mu) = \int_{\mu}^{1.2} e^{-wu} Q_k(u) u^i du + L_k^i(w,1.2) \tag{D25}$$

where the first and second terms on the right were evaluated by Gaussian quadrature and equation (D23), respectively.

General. - All G_{mnop} were evaluated to within ±4 in the sixth significant digit.

REFERENCES

1. Anon.: Proceedings of the NASA-University Conference on the Science and Technology of Space Exploration. NASA SP-11, Vol. 2, 1962, pp. 61-122.

2. Kascak, Albert F.; and Easley, Annie J.: Effect of Turbulent Mixing on Average Fuel Temperatures in a Gas-Core Nuclear Rocket Engine. NASA TN D-4882, 1968.

3. Slater, John C.: Quantum Theory of Molecules and Solids. Vol. 1. Electronic Structure of Molecules. McGraw-Hill Book Co., Inc., 1963.

4. Griffing, Virginia; and Vanderslice, Joseph T.: Studies of the Interaction between Stable Molecules and Atoms. IV. The Energy of the Linear H_4 Complex. J. Chem. Phys., vol. 23, no. 6, June 1955, pp. 1035-1038.

5. Griffing, Virginia; and Maček, Andrej: Studies of the Interaction between Stable Molecules and Atoms. III. A Molecular Orbital Treatment of the Quadratic Form of H_4. J. Chem. Phys., vol. 23, no. 6, June 1955, pp. 1029-1034.

6. Ruffa, A. R.; and Griffing, Virginia: Quantum Mechanical Study of the Hydrogen Bimolecular Exchange Reaction. J. Chem. Phys., vol. 36, no. 5, Mar. 1, 1962, pp. 1389-1394.

7. Taylor, R.: Complete Molecular Orbital Treatment of the System H_4. Proc. Phys. Soc. (London), Sec. A, vol. 64, pt. 3, Mar. 1951, pp. 249-260.

8. Magnasco, V.; and Musso, G. F.: Quantum Mechanics of the H_2 - H_2 Interaction. I. A Restricted Valence-Bond Approach. J. Chem. Phys., vol. 46, no. 10, May 15, 1967, pp. 4015-4025.

9. Magnasco, V.; and Musso, G. F.: Quantum Mechanics of the H_2 - H_2 Interaction. II. A Full Valence-Bond Calculation. J. Chem. Phys., vol. 47, no. 5, Sept. 1, 1967, pp. 1723-1730.

10. Magnasco, V.; and Musso, G. F.: Erratum: Quantum Mechanics of the H_2 - H_2 Interaction. II. A Full Valence-Bond Calculation. J. Chem. Phys., vol. 48, no. 6, Mar. 15, 1968, p. 2834.

11. Magnasco, V.; and Musso, G. F.: Quantum Mechanics of the H_2 - H_2 Interaction. IV. A Self-Consistent Group Calculation with Strong Orthogonal Group Functions. J. Chem. Phys., vol. 47, no. 11, Dec. 1, 1967, pp. 4629-4641.

12. Magnasco, V.; and Musso, G. F.: Quantum Mechanics of the H_2 - H_2 Interaction. V. The Importance of Intermolecular Charge-Transfer States. J. Chem. Phys., vol. 48, no. 6, Mar. 15, 1968, pp. 2657-2662.

13. Magnasco, V.; Musso, G. F.; and McWeeny, R.: Quantum Mechanics of the H_2 - H_2 Interaction. III. Nonorthogonal SCF-GF Calculations in the One-Configuration Approximation. J. Chem. Phys., vol. 47, no. 11, Dec. 1, 1967, pp. 4617-4628.

14. Schwartz, Maurice E.; and Schaad, L. J.: Ab Initio Studies of Small Molecules Using 1s Gaussian Basis Functions. III. LCGTO SCF MO Wavefunctions of the Three- and Four-Electron Systems He_2^+, He_2, and Linear H_3, H_4^+, H_4. J. Chem. Phys., vol. 48, no. 10, May 15, 1968, pp. 4709-4715.

15. Margenau, Henry: The Forces Between Hydrogen Molecules. Phys. Rev., vol. 64, no. 5 and 6, Sept. 1 and 15, 1943, pp. 131-147.

16. Evett, Arthur A.; and Margenau, Henry: The Forces Between Hydrogen Molecules. Phys. Rev., vol. 90, no. 6, Jun. 15, 1953, pp. 1021-1023.

17. Mason, Edward A.; and Hirschfelder, Joseph O.: Short-Range Intermolecular Forces. II. H_2 - H_2 and H_2 - H. J. Chem. Phys., vol. 26, no. 4, Apr. 1957, pp. 756-766.

18. Vanderslice, Joseph T.; and Mason, Edward A.: Interaction Energies for the H - H_2 and H_2 - H_2 System. J. Chem. Phys., vol. 33, no. 2, Aug. 1960, pp. 492-494.

19. Abrams, Rochelle B.; Patel, Jashbhai C.; and Ellison, Frank O.: Methods of Diatomics-in-Molecules. IX. Ground and Excited States of H_4 and the H_2, H_2 Bimolecular Exchange Reaction. J. Chem. Phys., vol. 49, no. 1, July 1, 1968, pp. 450-457.

20. Van Kranendonk, J.; and Kiss, Z. J.: Theory of the Pressure-Induced Rotational Spectrum of Hydrogen. Can. J. Phys., vol. 37, no. 10, Oct. 1959, pp. 1187-1198.

21. Guevara, F. A.; and Wageman, W. E.: Measurement of Helium and Hydrogen Viscosities to 2340 K. Rep. LA-3319, Los Alamos Scientific Lab., Sept. 2, 1965.

22. Fisher, B. B.: Calculations of the Thermal Properties of Hydrogen. Rep. LA-3364, Los Alamos Scientific Lab., Apr. 20, 1966.

23. McWeeny, R.: The Valence Bond Theory of Molecular Structure. I. Orbital Theories and the Valence-Bond Method. Proc. Roy. Soc. (London), Ser. A, vol. 223, no. 1152, Apr. 7, 1954, pp. 63-79.

24. McWeeny, R.: The Valence-Bond Theory of Molecular Structure. II. Reformulation of the Theory. Proc. Roy. Soc. (London), Ser. A, vol. 223, no. 1154, May 6, 1954, pp. 306-323.

25. Weinbaum, Sidney: The Normal State of the Hydrogen Molecule. J. Chem. Phys., vol. 1, no. 8, Aug. 1933, pp. 593-596.

26. Spindler, R. J., Jr.: Franck-Condon Factors for Band Systems of Molecular Hydrogen I. The $\left(B\ ^1\Sigma_u^+ - X\ ^1\Sigma_g^+\right)$, $\left(I\ ^1\Pi_g - B\ ^1\Sigma_u^+\right)$ and $\left(d^3\Pi_u - a\ ^3\Sigma_g^+\right)$ Systems. J. Quant. Spectrosc. Radiat. Transfer, vol. 9, no. 5, May 1969, pp. 597-626.

27. Spindler, Robert J., Jr.: Optical Functions for Molecular Hydrogen. Rep. AVSSD-0287-66RR, Avco Corp. (NASA CR-72107), Sept. 30, 1966.

28. Löwdin, Per-Olov: On a Quantum Theory of Cohesive Properties of Solids. Adv. Phys., vol. 5, no. 17, Jan. 1956, pp. 3-172.

29. Magnasco, Valerio; and Musso, Gianfranco: Population Analysis of Many Configuration Wave Functions. Atti dell Accademia Ligure di Scienze e Lettere, vol. 22, 1965, pp. 383-389.

30. Slater, J. C.: Molecular Energy Levels and Valence Bonds. Phys. Rev., vol. 38, no. 6, Sept. 15, 1931, pp. 1109-1144.

31. Slater, John C.: Quantum Theory of Atomic Structure. Vol. 1. McGraw-Hill Book Co., Inc., 1960, pp. 113-119.

32. Hirschfelder, Joseph O.; Curtiss, Charles F.; and Bird, R. Byron: Molecular Theory of Gases and Liquids. John Wiley & Sons, Inc., 1954.

33. Dellepiane, Giovanna; Ferro, Dino R.; and Magnasco, Valerio: Multicentre Molecular Integrals in Theoretical Chemistry. Note III: A Program for the Evaluation of the Exponential Integral Function. La Ricerca Scientifica, IIA, vol. 3, no. 8, Dec. 1963, pp. 1195-1200.

34. Kolos, W.; and Wolniewicz, L.: Potential-Energy Curves for the $X\ ^1\Sigma_g^+$, $b\ ^3\Sigma_u^+$, and $C\ ^1\Pi_u$ States of the Hydrogen Molecule. J. Chem. Phys. vol. 43, no. 7, Oct. 1, 1965, pp. 2429-2441.

35. Kolos, W.; and Wolniewicz, L.: Polarizability of the Hydrogen Molecule. J. Chem. Phys., vol. 46, no. 4, Feb. 15, 1967, pp. 1426-1432.

36. Magnasco, Valerio; and Dellepiane, Giovanna: Multicentre Molecular Integrals in Theoretical Chemistry. Note I: On the Evaluation of 3-centre Nuclear Attraction and Coulomb Integrals Involving 1s Atomic Orbitals. La Ricerca Scientifica, IIA, vol. 3, no. 8, Dec. 1963, pp. 1173-1186.

37. Magnasco, Valerio; and Dellepiane, Giovanna: Multicentre Molecular Integrals in Theoretical Chemistry. Note IV: On the Evaluation of 3-Centre Exchange and 4-Centre Integrals over 1s Atomic Orbitals. La Ricerca Scientifica, IIA, vol. 4, no. 3, July 1964, pp. 275-288.

38. Rosen, N.: Calculation of Interaction between Atoms with s-Electrons. Phys. Rev. vol. 38, no. 2, July 15, 1931, pp. 255-276.

39. James, Hubert M.; and Coolidge, Albert Sprague: The Ground State of the Hydrogen Molecule. J. Chem. Phys., vol. 1, no. 12, Dec. 1933, pp. 825-835.

40. Rosen, N.: The Normal State of the Hydrogen Molecule. Phys. Rev., vol. 38, no. 12, Dec. 15, 1931, pp. 2099-2114.

NASA-Langley, 1969 —— 24 E-5075

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
WASHINGTON, D. C. 20546

OFFICIAL BUSINESS

FIRST CLASS MAIL

POSTAGE AND FEES PAID
NATIONAL AERONAUTICS AND
SPACE ADMINISTRATION

POSTMASTER: If Undeliverable (Section 158 Postal Manual) Do Not Return

"The aeronautical and space activities of the United States shall be conducted so as to contribute . . . to the expansion of human knowledge of phenomena in the atmosphere and space. The Administration shall provide for the widest practicable and appropriate dissemination of information concerning its activities and the results thereof."

—NATIONAL AERONAUTICS AND SPACE ACT OF 1958

NASA SCIENTIFIC AND TECHNICAL PUBLICATIONS

TECHNICAL REPORTS: Scientific and technical information considered important, complete, and a lasting contribution to existing knowledge.

TECHNICAL NOTES: Information less broad in scope but nevertheless of importance as a contribution to existing knowledge.

TECHNICAL MEMORANDUMS: Information receiving limited distribution because of preliminary data, security classification, or other reasons.

CONTRACTOR REPORTS: Scientific and technical information generated under a NASA contract or grant and considered an important contribution to existing knowledge.

TECHNICAL TRANSLATIONS: Information published in a foreign language considered to merit NASA distribution in English.

SPECIAL PUBLICATIONS: Information derived from or of value to NASA activities. Publications include conference proceedings, monographs, data compilations, handbooks, sourcebooks, and special bibliographies.

TECHNOLOGY UTILIZATION PUBLICATIONS: Information on technology used by NASA that may be of particular interest in commercial and other non-aerospace applications. Publications include Tech Briefs, Technology Utilization Reports and Notes, and Technology Surveys.

Details on the availability of these publications may be obtained from:

SCIENTIFIC AND TECHNICAL INFORMATION DIVISION

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

Washington, D.C. 20546